Volume XLIII January-February 1948 Number 1

Economic Geology

and the

Bulletin of the Society of Economic Geologists

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PUBLISHED SEMI-QUARTERLY

Five Dollars a Year, One Dollar a Copy

THE ECONOMIC GEOLOGY PUBLISHING COMPANY

Printed by Lancaster Press, Inc., Prince and Lemon Streets, Lancaster, Pa.

Entered as second-class matter, March 30, 1906, at the Post Office at Lancaster, Pa., under the Act of Congress of March 3, 1879

Economic Geology

and the

Bulletin of the Society of Economic Geologists

Issued Semi-Quarterly and sent to subscribers on or about the following dates: February 1, March 15, May 1, June 15, August 1, September 15, November 1, December 15.

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Indexed in the Industrial Art Series.

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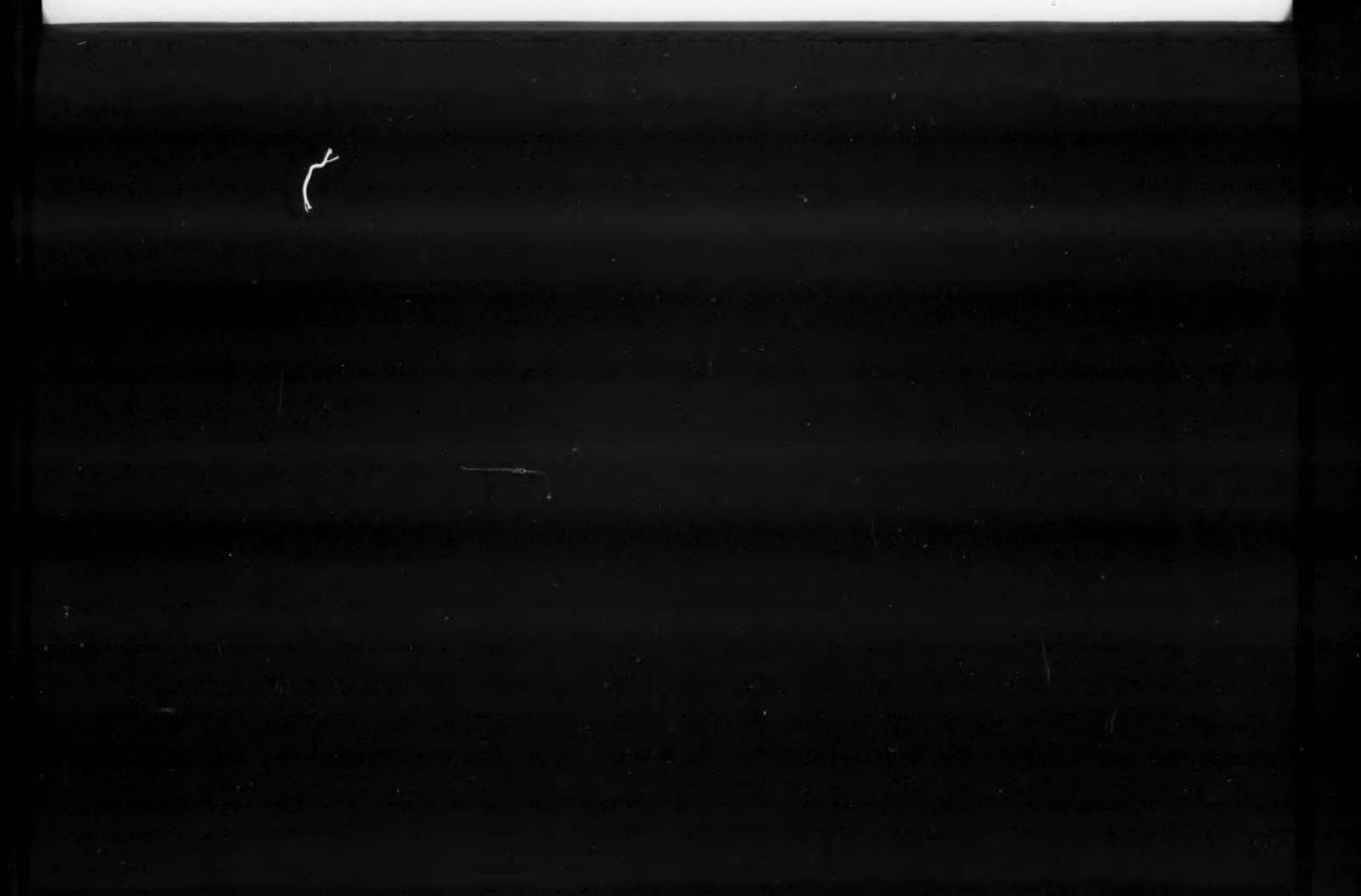

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VOL. XLIII JANUARY–FEBRUARY, 1948 No. 1

GEOTHERMAL GRADIENTS, RECENT CLIMATIC CHANGES, AND RATE OF SULFIDE OXIDATION IN THE SAN MANUEL DISTRICT, ARIZONA.[1]

T. S. LOVERING.

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ABSTRACT.

Thermal gradients were measured in eleven churn drill holes in the San Manuel district, 40 miles north of Tucson, Arizona, to determine if possible whether oxidizing sulfides undisturbed by mining operations gave off measurable amounts of heat. Nearly all the geothermal gradients have two inflection points and many of them have three.

Comparison of the gradient in different rocks in the same hole showed that the conductivity of the different wall rocks, both wet and dry, differs by such small amounts that the effect on the thermal gradient was inconspicuous with the instruments used. The thermal conductivities of three representative samples were determined by Francis Birch and range from .0053 to .0085 ($cal.cm^{-1}\ sec^{-1}$).

Historical records and tree rings both indicate change from moist to dry climate about 65 years ago, but the accompanying temperature changes

[1] Printed by permission of the Director, U. S. Geological Survey.

are unknown. The inflections in the depth-temperature curves above 500-foot depths harmonize with the assumption that the average surface temperature increased when the arid cycle began. The preceding moist climate had apparently continued without interruption from 1600 to about 1880 and had succeeded a devastating drought that lasted from 1570 to 1600. If this early drought was accompanied by a warmer climate the inflection on the depth-temperature curves would now be found at a depth of about 800 feet, approximately where the deepest inflections are found. Aside from these inflections, believed assignable to climatic changes, the most marked inflection is in the gradients of the holes where sulfides are at or above water level, and the departure in each of these indicates a heat source in the sulfides. The difference in slope above and below the inflection related to the sulfide zone is used to calculate the rate of oxidation of pyrite. The gradient due to oxidation is from 0.4° to 0.6° F per 100 feet and the heat liberated under each square centimeter of surface by oxidizing pyrite is approximately 28 calories per year. At this rate about 40,000 years would be required for the complete oxidation of the pyrite. The rocks are strongly fractured but the fractures are tight and the rock mass appears to have a low permeability; if more open fractures were present the rate of oxidation would probably be many times as fast and the gradient due to oxidation would then be several times as steep. In other localities horizontal gradients of several degrees per hundred feet have been observed underground near vertical sulfide veins, which are commonly marked by thermal "highs" 15° to 40° F above the normal rock temperature. Calculations show that more than 95 percent of the oxygen necessary for converting sulfide to oxide must come from air entering and leaving the voids as a result of changing barometric pressure.

Using the least distorted geothermal gradients and the conductivity of the altered rocks as determined by Francis Birch, the heat flow where no oxidation is taking place is apparently equivalent to not less than 30 nor more than 46 calories per square centimeter per year.

INTRODUCTION AND ACKNOWLEDGMENTS.

THE San Manuel property, now leased and being explored by Magma Copper Company, is 9 miles north of Oracle, Arizona, and about 40 miles north of Tucson. It was studied jointly by the U. S. Bureau of Mines and the U. S. Geological Survey in 1943–44 as a part of the wartime program of strategic minerals investigations.

In December 1944 the writer measured temperatures in 11 deep bore holes which had been drilled in this area for the Bureau of Mines. The petrographic examination of the drill cuttings was made chiefly by G. M. Schwartz of the U. S. Geological Survey and the logs which he prepared of the holes were an invaluable aid in the interpretation of the geothermal gradients. The determination of the thermal conductivity of the altered rocks was carried out by Francis Birch at Harvard University. He has generously made the results available for this study. The writer also wishes to acknowledge the help received from M. V. Denny, curator of the Mineralogy Department, University of Michigan, who determined bulk and powder densities of several specimens of altered rock. E. T. McKnight and Cecil Spicer, of the U. S. Geological Survey, both made valuable suggestions as to the material incorporated in this paper.

GEOLOGY.

As shown by the fourteen deep churn drill holes drilled prior to 1945 by the Bureau of Mines, strongly mineralized quartz monzonite and monzonite porphyry lie beneath the Gila conglomerate (probably Pliocene and Pleistocene age). A substantial chalcocite zone carrying about one percent copper is present and is underlain by ore carrying chalcopyrite and bornite. Beneath this zone, which dips south, low-grade, disseminated pyrite occurs in sericitized monzonite porphyry and quartz monzonite to a substantial depth. The transitions from oxidized zone to chalcocite zone and to primary sulfides as determined by Schwartz are relatively abrupt.[2] The chalcocite zone is tilted and the present water table is an irregular surface from 600 to 700 feet below the topographic surface in all but hole 13, where water was reached at 245 feet. Two of the holes (nos. 9 and 11) cut the sulfide zone more than 100 feet above water table, but others did not penetrate the zone until several hundred feet below the water table. The topography and location of the holes are shown in Fig. 1. The chalcocite zone is not related to the present surface or the present water table, and the range in depth of the sulfides is especially favorable for a critical study of the heat generated during their oxidation.

GEOTHERMAL GRADIENTS.

Temperatures were measured in the drill holes with the temperature machine designed by C. E. Van Orstrand,[3] formerly Chief Physicist of the U. S. Geological Survey. Mercury maximum thermometers reading in degrees Fahrenheit were used and compared with a calibrated standard Fahrenheit thermometer. By means of a specially designed ocular it was possible to estimate temperatures to tenths of a degree with an error probably not more than one tenth of a degree. If the temperature of the thermometer case differed by ten degrees or more from that of the rock wall, the cooling effect of the case lowered the observed temperature perceptibly and gave erroneous results. It was necessary to hold the instrument some distance above the point to be recorded until thermal equilibrium was nearly established before lowering it to the desired position and again waiting for thermal equilibrium to take place. Using this technique, it was found that temperatures could be rechecked to within a tenth of a degree in a much shorter time than with the one-stop technique advised by Van Orstrand. To obtain equilibrium readings when the thermometer case was less than 10° F below its surroundings required about 45 minutes for air temperatures and about 10 minutes for water temperatures.

The data for the eleven drill holes are shown in Table 1.

All gradients are believed to be satisfactory except that of hole 13, where very erratic and unreproducible temperatures indicate a marked stirring of

[2] Schwartz, G. M.: Geology of the San Manuel area, Pinal County, Arizona. U. S. Geol. Survey, Strategic Minerals Investigations, Preliminary Map 3–180.

[3] Van Orstrand, C. E.: Description of apparatus for the measurement of temperatures in deep bore holes, Pt. II, Earth temperatures in oil fields. Am. Petroleum Inst. Production Bull. 205, 1930.

TABLE 1.

TEREMPATURES MEASURED IN SAN MANUEL CHURN DRILL HOLES, DECEMBER 1944.

Hole No.	Feet	° F
2	100	72.4
	300	73.9
	500	76.1
	700	78.0
	900	79.9
	945	80.2
	(Surface temp. 71.7° F [1])	
4	100	73.4
	250	74.0
	300	74.2
	350	74.5
	420	75.3
	500	76.4
	650	78.0
	750	78.8
	835	79.6
	(Surface temp. 73.0° F [1])	
5	100	71.5
	300	74.1
	450	75.7
	620	77.7
	740	78.7
	(Surface temp. 70.2° F [1])	
6	100	72.7
	300	74.4
	500	76.1
	650	77.8
	750	78.8
	825	79.4
	(Surface temp. 71.8° F [1])	
7	100	73.2
	400	75.2
	420	75.3
	550	76.5
	700	78.1
	850	79.6
	950	80.1
	(Surface temp. 72.5° F [1])	
8	100	71.9
	300	74.1
	500	76.2
	620	77.7
	710	78.4
	(Surface temp. 70.8° F [1])	
9	100	72.0
	250	73.1
	400	74.4
	500	75.1
	600	76.4
	720	77.2
	(Surface temp. 71.2° F [1])	
10	100	73.6
	250	74.1
	400	75.0
	600	76.3
	745	77.2
	(Surface temp. 73.2° F [1])	
11	50	69.6
	100	71.0
	175	72.3
	200	72.8
	250	73.3
	350	74.5
	400	75.0
	500	76.1
	600	77.2
	700	78.0
	780	78.4
	(Surface temp. 68.3° F [1])	
12	100	73.1
	200	73.8
	300	74.6
	450	76.0
	550	77.1
	650	78.3
	820	79.8
	(Surface temp. 72.4° F [1])	
13	100	72.9
	270	74.1
	500	74.9
	500	75.7
	500	75.7
	625	75.7
	750	78.1
	1000	82.7
	(Surface temp. 72.3° F [1])	

[1] Mean annual surface temperature indicated by gradient between first two points at which temperatures were measured.

the water; a constant gurgling noise from this hole suggested a gas seepage into the water and therefore the temperatures observed were not used in this study.

Seven of the depth-temperature curves shown in Fig. 2 show inflection points above 400 feet and a few show others at deeper levels. Some of the

inflections seem related to the transition from oxidized zone to sulfide zone but for several of the gradients no such relation exists.

Changes in the slope of a geothermal gradient can be caused by (1) differences in the conductivity of the rocks; (2) changes in surface temperature; (3) subsurface heat sources; and (4) subsurface heat sinks.

Relative Conductivity.—The quantity of heat Q passing through a unit volume of a substance in unit time equals mk, where m is temperature gradient and k is the thermal conductivity. If the geothermal gradient is in equilibrium and, as a consequence, the same quantity of heat passes through all the section, the gradients in different rocks will be inversely proportional to their thermal conductivities. Thus a gradient of 2° per 100 feet in quartzite would give way abruptly to a gradient of 8° per 100 feet in a rock such as shale, having only a fourth of the thermal conductivity of the quartzite.

TABLE 2.

THERMAL DATA ON ALTERED ROCKS FROM SAN MANUEL DISTRICT:

P = pressure (lb in^{-2}); t = temperature, °C; k = conductivity (cal. cm^{-1} sec^{-1} deg^{-1}); $d(bk)$ = bulk density; $d(pd)$ = powder density; sp.h. = specific heat (cal. gm^{-1}); h^2 = diffusivity (c.g.s.).

Specimen	P	t	k	$d(bk)$	$d(pd)$	sp.h.	h^2
1	0	40	.00715				.018
	0	40	.0072				.018
	500	40	.0082				.019
	500	40	.0083				.019
	1500	40	.00857				.020
	1500	40	.0086				.020
	0	25		2.454	2.704		
	0	15				.175	
2	0	40	.00475				.011
	1000	40	.0053				.013
	1000	40	.00535				.013
	1500	40	.00535				.013
	1500	40	.00543				.013
	0	25		2.475	2.593		
	0	15				.170	
3	0	40	.0081				.019
	0	40	.0083				.020
	1500	40	.0085				.020
	1500	40	.0085				.020
	1500	40	.0086				.021
	1500	40	.0086				.021
	0	25		2.544	2.648		
	0	15				.164	

Three samples of rock were selected from Schwartz's collection as representative of the probable range in rock and alteration types, and their thermal constants were determined (Table 2). Birch ascertained the thermal conductivity with a possible error of not more than one percent; Denny obtained values for the bulk and powder density that are believed accurate within 0.1 percent; and the writer determined the specific heats of the specimens with a probable error of less than 2 percent.

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Specimen 1 is from the surface on Red Hill and is a highly altered, coarse-grained quartz monzonite; except for original quartz, the rock is almost completely converted to hydromica and sericite with moderately abundant hematite pseudomorphs after pyrite. The specimen contains many microvugs and, except for being oxidized, is typical of the pyrite-hydromica alteration zone that underlies the disseminated ore.

Specimen 2 is an unweathered monzonite porphyry from hole 73 taken at a depth of 735 feet and is a medium-grained, slightly sericitized rock, typical of the outer fringe of hydrothermal alteration. The abundant plagioclase phenocrysts contain less than 10 percent sericite; the other minerals and the groundmass are almost fresh.

Specimen 3 is an unweathered monzonite porphyry from hole 15 taken at 1,900 feet. It is a medium-grained, strongly sericitized, moderately silicified rock containing some adularia and abundant pyrite; it has many microvugs and some macrovugs as much as 2 by 10 mm. in diameter. The alteration is typical of that found in the zone of disseminated ore.

It is interesting to note that the conductivity and diffusivity of the altered quartz monzonite are almost identical with those of the altered monzonite porphyry, and are about 50 percent higher in value than those of the fresh porphyry. As all the temperature gradients measured by the writer were in altered rock, the data in Table 1 indicate that the conductivity of the wall rocks may be expected to approximate 0.008 in all the drill holes studied.

The conductivity of a rock is usually greater when it is wet than when it is dry. The meager data recorded suggest that the increase ranges from about 10 percent for rocks of low porosity to about 35 percent for sandstones having a porosity of 22 percent.[4] An increase of 10 percent would hardly be perceptible in the San Manuel gradients unless measured with more sensitive instruments than were available. There is no change of geothermal gradient in the oxidized zone at the water table in holes 7 and 10, and the change in conductivity is therefore probably not more than 10 percent.

As pyrite is about three times as conductive as hematite, the oxidized zone should be a poorer conductor than the sulfide zone. The total content of pyrite in the sulfide zone is about 5 percent by weight. If unpyritized altered rock has a conductivity of 0.008, the addition of 5 percent pyrite would increase the average conductivity to 0.00819. A similar volume of hematite would increase the conductivity to 0.00814. (See calculations, p. 16.) Thus the difference in conductivity between the oxidized and sulfide zones should be negligible; the conductivity of specimens 1 and 3, Table 2, and the thermal gradients of holes 2 and 6, shown in Fig. 2, bear out this conclusion.

The bedrock is made up chiefly of coarse-grained quartz monzonite, medium-grained monzonite porphyry, and the Gila conglomerate, which here is composed of coarse subangular fragments of the quartz monzonite and later volcanics in an arkosic matrix. Fresh quartz monzonite probably has a higher conductivity than fresh monzonite porphyry, if published values of thermal constants for comparable rocks may be used as a guide, and thus

[4] Birch, Francis, Schairer, J. F., and Spicer, H. C.: Handbook of physical constants, Geol. Soc. America Special Paper 36, p. 258, 1942.

smaller geothermal gradients would be expected in normal quartz monzonite. As noted earlier, however, the intense hydrothermal alteration characteristic of the San Manuel area has tended to reduce both rocks to the same thermal constants.[5]

A geothermal gradient of 1° F per 100 feet in strongly altered monzonite porphyry would be in equilibrium with a gradient of about 1.6° F in fresh monzonite porphyry. Abrupt variations in the degree of alteration may explain some of the small kinks in the depth-temperature curves of Fig. 2, but if the probable error of temperature measurement (±0.1° F) is taken into account, the data for all the holes fall on relatively smooth curves and changes in formation are not reflected in the geothermal gradient. The lack of relation between wall rock and temperature gradient is illustrated by hole 11 (Fig. 2); there is a flattening[6] in the gradient at 200 feet where the hole passes from monzonite porphyry into quartz monzonite but on the other hand there is again a flattening of the geothermal gradient at 575 feet where the hole passes out of the quartz monzonite and back into the monzonite porphyry. Neither of the changes in slope is as great as those occurring entirely within the boundaries of one formation, and both are apparently parts of larger inflections related to other factors. The slope of the geothermal gradient in hole 9 (Fig. 2) shows almost no change where the hole passes from monzonite porphyry to quartz monzonite at 275 feet; no change can be seen in the geothermal gradient of hole 6 (Fig. 2) at 225 feet where it passes from the Gila conglomerate into monzonite porphyry. It seems evident that the differences in thermal conductivity of the hydrothermally altered formations and the later Gila conglomerate are small.

Changes in Surface Temperature.—Erosion is constantly modifying the surface but if the process is slow the geothermal gradient will be little affected. A rapid incision of valleys and the resulting concentration of runoff in them may lower the surface temperatue locally and cause a readjustment and consequently a distortion of the geothermal gradient. The present mean surface temperature indicated by the San Manuel gradients is closely related to topographic features and to the relative exposure to the sun (Fig. 1).

The north-facing slope of the ridge southeast of Red Hill has fewer hours of shade per day than the bottom of the recently cut, steep-sided, east-west trending arroyo at its foot. This slope, however, is far less exposed to the sun than the crest of the ridge and the south slopes. The lowest mean surface temperature (68.3° F) is at hole 11 which is at the bottom of the steep-sided, easterly trending gully; the next lowest (70.2° F and 70.8° F) are for holes 5 and 8 which are on the north-facing slope of this gully about 50 feet from the bottom. The highest mean surface temperatures (73.0° and 73.2° F) are found at holes 4 and 10, located on ridge crests.

Most of the depth-temperature curves show an inflection at a depth of 250 to 400 feet that is clearly unrelated to the character of the bedrock or to sul-

[5] Op. cit., pp. 251–258.

[6] The word "flattening" is used in the sense customary when speaking of geothermal gradients, a slower increase in temperature per unit of depth, but such a change is indicated in Fig. 2 by a steeper part of the curve because they have been drawn in reference to the Y axis instead, as is customary, in reference to the X axis.

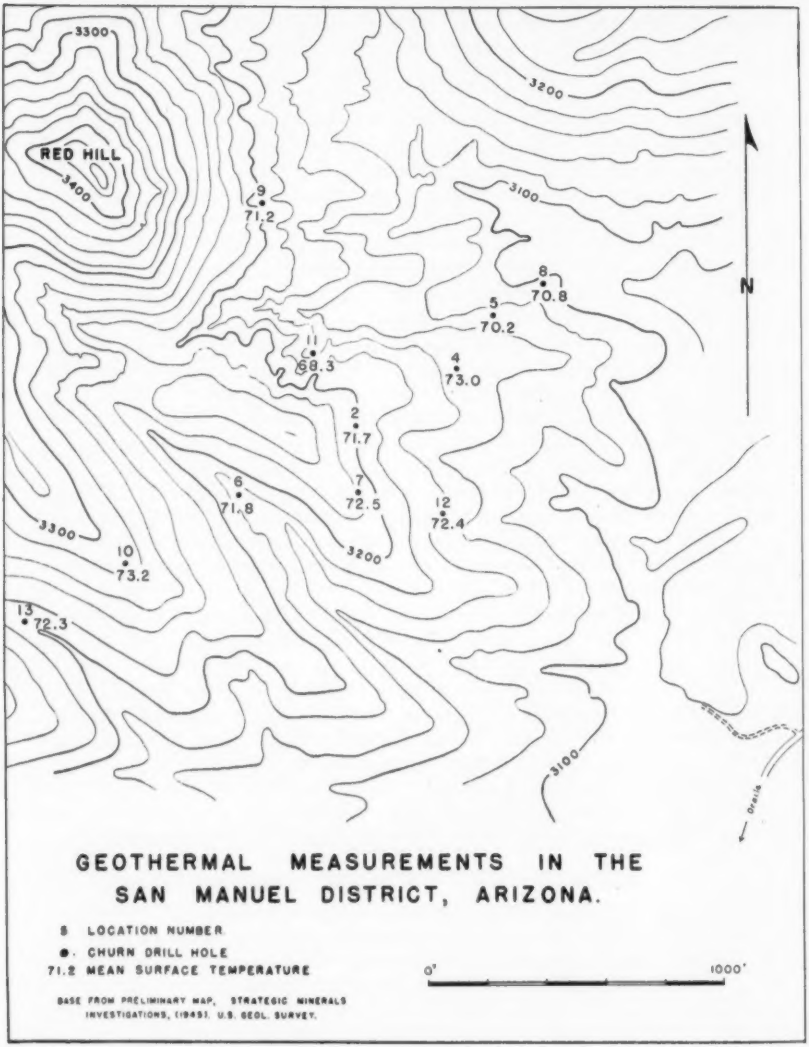


FIG. 1. Map showing locations of geothermal measurements in the San Manuel area.

fides and may reflect a climatic change. Extrapolation of the nearly straight line geothermal gradient in all the holes below this inflection suggests a former surface temperature of 70° to 71° F. The smallness of the inflection for the geothermal gradients of holes 5 and 8 on the north-facing slope of the recently cut arroyo shows that any climatic change had little effect on this specific part of the area. The indicated cooler temperature that now obtains in the bottom of the recently cut arroyo suggests that the shade cast by the steep banks may be a new factor coinciding with a climatic change which caused arroyo cutting to start.

According to Bryan,[7] the present arroyo-cutting cycle in the San Pedro valley, where the San Manuel district lies, began about 1883. Prior to that time the San Pedro wash had been covered with grass for centuries and since then none has grown in this area. The change in climate is also recorded by a sharp narrowing of tree rings throughout the Southwest. The work on tree rings of A. E. Douglas and his co-workers, as reported by Schuleman,[8] shows that periods of severe drought have recurred about every third century since 700 A.D. After a devastating drought from 1570 to 1600, the Southwest enjoyed a comparatively moist and uniform climate until the middle of the nineteenth century when a gradual trend toward desiccation began. A moisture minimum in 1880 ushered in a period of marked aridity which has lasted to the present time, broken only by many storm years during the first two decades of the present century. The character of the precipitation during the storm years was such that the land continued bare of grass. No direct data on climatic temperatures are given by tree rings, but it is probable that the average temperature of the surface when covered with grass would be appreciably lower than in times of drought when bare ground faced the sun. Thus the time of the last major climatic change seems fairly well fixed as approximately 1880, some 64 years prior to the date of temperature measurement.

As noted several years ago by Hotchkiss and Ingersoll,[9] it is possible to calculate the effect of climatic changes on geothermal gradients if sufficient data are available. For such calculations (see p. 17), it is necessary to know the thermal diffusivity of the rocks, the surface temperatures as a function of time, and the gradient at the start of the period under consideration.

The diffusivity of the sericitized rocks can be calculated with reasonable accuracy from the determinations made by Birch, and almost certainly lies between 0.017 and 0.021, so that a figure of 0.019 is probably correct within 10 percent.

Unfortunately, none of the other factors is known accurately, but the probable variation of each can be estimated within reasonably small limits. Even if the figures assumed for these factors make it possible to calculate depth-temperature curves that coincide with those of the drill holes, this would not

[7] Bryan, Kirk: Date of channel trenching (arroyo cutting) in the arid southwest. Science, Vol. 62, pp. 338–344, 1925.

[8] Schuleman, Edward: Nineteen centuries of rainfall in the southwest. Bull. Am. Meteorological Soc., Vol. 19, pp. 211–215, 1938.

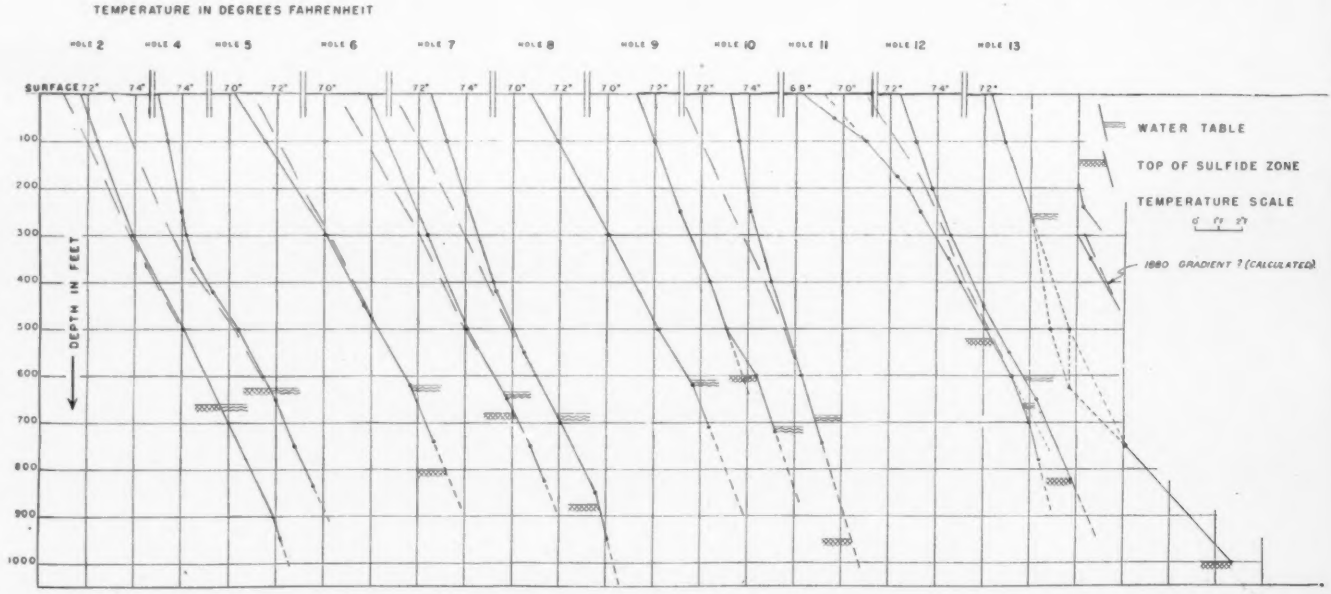
[9] Hotchkiss, W. O., and Ingersoll, L. R.: Postglacial time calculations from recent geothermal gradient determinations in the Calumet copper mines. Jour. Geology, Vol. 42, pp. 113–122, 1943.

prove that the assumed factors were correct. It would indicate, however, that the assumptions could be reasonably close to actual conditions.

As none of the depth-temperature curves are straight lines, it is important to know whether the variations in surface temperature during the past few centuries may plausibly account for some of the inflections and if so, which inflections are most likely to be correlated with the climatic history.

The mean annual surface temperatures at present range from about 68° F in the bottom of the steep-sided shady arroyo to a little more than 73° F on the south-facing slopes. It is unlikely that the average temperature differed as much when grass covered the hills but the actual temperatures are unknown. The only gradient shown in Fig. 2 that approximates a straight line is that for hole 8, about 80 feet south of the mouth of the east-west arroyo. The lack of strong inflections suggests that the average surface temperature here (70.8° F) has been nearly constant for a long time, and it is to be expected that the present temperature on this north-facing slope would be closer to that of the preceding somewhat humid cycle than that of the south-facing slopes. If it is assumed for trial calculation that the rocks have a diffusivity of 0.019 and that the average temperature prior to 1880 was about 71° F, the gradient existing at that time can be calculated from the present one (see calculations, p. 19). The results of such a calculation are shown in Fig. 2. The inflections above 500 feet are all greatly minimized and in several holes the "1880 gradient?" approximates a straight line with a slope almost identical with that of the present apparently undisturbed gradient in hole 8. This coincidence makes it plausible to assume that the inflections above 500 feet reflect the local thermal vicissitudes since the major climatic change of 1880. Calculation shows that if higher temperatures accompanied the drought of 1570–1600, the flattening of the gradients which would have been induced near the surface at that time would now appear as a minor steplike inflection at a depth of about 800 feet. The original near-surface change in gradient would progress downward as a "heat wave" of constantly diminishing intensity and might be imperceptible at such a depth if the original change in surface temperature had been small.

If the surface temperature prior to 1570 had averaged 71° F for a long period of time and temperature gradients of 1° F per 100 feet were uniform to substantial depth, an increase in mean annual temperature to approximately 74° F (an increase of 1.65° C) for 30 years followed by a return to an average temperature of 71° lasting till the present—as at hole 8—would be reflected by a maximum deflection from a straight line gradient of about 0.06° F, at a depth of about 800 feet (see calculations, p. 19). A higher average temperature between 1,570 and 1,600 would cause a larger inflection at approximately the same depth. Most of the holes were closed above 800 feet but in holes 2 and 7 temperatures were taken at greater depth; the gradients in both suggest a minor inflection at about 850 feet. It is possible that this flattening of the gradient marks the present position of a "heat wave" generated during the Great Drought that closed the sixteenth century in the Southwest, but many more temperature measurements in other holes extending below 1,000 feet would be needed before this possibility could be appraised. Apparently



TEMPERATURE MEASURED IN BUREAU OF MINES CHURN DRILL HOLES, DECEMBER, 1944.

FIG. 2.

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only the inflections at about 400 and 800 feet can be explained by the major climatic changes during the past few centuries. Other inflections show a remarkably close relation to the upper limits of sulfides. These are especially evident in hole 9 where the sulfides are above water level (Fig. 2). Without exception these inflections are of the type that would be caused by a heat source in the sulfides.

Heat Flow Due to Internal Heat of the Earth.—The straight line gradient of hole 8 is 1.09° F per 100 feet; the mean of the "1880 gradients?" (Fig. 2) of all the holes is 1.05° F per 100 feet with a maximum deviation of − 0.25° F (hole 9). The present gradient between 500 and 700 feet should be less disturbed by climatic changes than at shallower depths or at somewhat greater depth. The average gradient of all holes in this interval is 1.0° F per 100 feet of depth, with one deviation of − 0.35° F (hole 10); the others range between 1.0° F and 1.1° F. If only those holes in which the top of the sulfide zone is more than 100 feet below the water table are considered (holes 5, 7, 8, and 10), the gradients in the interval 500 to 700 feet are found to be 1.0°, 1.05°, 1.05° and .65° F per 100 feet. There is usually a small amount of residual sulfide in the oxidized zone—commonly less than 0.3 percent pyrite if all sulfur is assigned to this mineral, and so there may be a small contribution of heat from this source. It is believed that the normal gradient undisturbed by exothermic chemical reactions or climatic changes lies between 0.65° and 1.0° F per 100 feet. Using the conductivity of 0.008 determined by Birch, the amount of heat flowing to the surface in the San Manuel area exclusive of any contributed by oxidation is calculated to be not less than $.95 \times 10^{-6}$ cal.cm^{-2} sec^{-1} nor more than 1.46×10^{-6} cal.cm^{-2} sec^{-1}, equivalent to a minimum of 30 and a maximum of 46 calories per square centimeter per year. These results compare closely with those found in the few other localities in the world where the heat flow and conductivity of the rocks have been correlated.[10]

Heat Sources and Heat Sinks.—Water circulating actively along underground channels would act as a heat source or a heat sink depending on whether its temperature was above or below that appropriate to the rock under the influence of the normal geothermal gradient. With the exception of hole 13 where conflicting readings were obtained, no evidence of this type of heat source or heat sink was found.

It is quite possible, however, that the low surface temperature of hole 11 is caused by a concentration of runoff in the arroyo where it is located. As the amount of moisture fed to the porous underlying bed rock is larger than on the hill slopes, it probably acts as a heat sink at shallow depths and thus causes the abnormally steep initial gradient and low temperatures.

Endothermic reactions are unimportant in the zone of weathering so far as known, and as no other types of heat sink seem probable in the San Manuel district this factor was not considered further.

The distortion of the geothermal gradient near the top of the main sulfide zone where it is above or close to water level seems best explained by a heat

[10] Birch, Francis, Schairer, J. F. and Spicer, H. C.: Handbook of physical constants. Spec. Pap. 36, Geol. Soc. America, pp. 201–202, 1942.

source in this part of the section. Oxidation of pyrite to limonite is an exothermic reaction which liberates approximately 2,864 gm cal per gm of pyrite (see p. 19).

If the heat source were a widespread layer of oxidizing disseminated pyrite and had been generating heat at a uniform rate for several centuries, the gradient would be essentially uniform from water level to the surface, even though the sulfides were present some distance above the zone of saturation, as in hole 11, and the inflection would be near the water table. Where the start of oxidation was relatively recent and equilibrium had not been established the inflection would be just above the sulfide, as in hole 9.

The amount of heat generated during the oxidation of a tabular body of pyrite would be reflected by the gradient above the ore and its steepness would be proportional to the rate of oxidation, since for unit volume $Q = mk$, and $m = Q/k$ where Q = cal per sec (rate of oxidation), m = geothermal gradient, and k = conductivity.

The rate of oxidation is related to the composition and physical state of the sulfides, to the permeability of the mass and to its depth. Mixed sulfides oxidize more readily than do monomineralic sulfide masses, and the presence of small amounts of certain impurities also accelerates oxidation. Fractured material has a larger surface exposed to attack and the fractures also make it more permeable to air and water. Oxygen is supplied by both air and aqueous solutions; every change in barometric pressure pumps air into or out of the voids that communicate with the earth's surface. In arid and semi-arid regions where the water table is deep, this slow breathing of the earth probably causes more oxidation than the downward movement of ground water. To oxidize one gm of pyrite with the oxygen dissolved under normal atmospheric pressure in water at 50° F would require a volume of 90,900 cc of water; the same amount of oxygen would be contained in 3,960 cc of air.

The amount of oxygen in the air pumped in and out by changing barometric pressure would be largest near the surface and thus the rate of oxidation might diminish appreciably with depth. However, the rate of oxidation by either air or water at any depth would be closely related to the permeability of the rocks.

In the San Manuel district the altered sulfide-bearing monzonite porphyry and quartz monzonite are crisscrossed with innumerable tight fractures and are cut by a few strong gouge-filled faults. The permeability of this type of fractured rock is believed low but no tests have been made on the rocks of the district. The depth to the sulfide, low permeability of the rocks, and small amount of sulfide present here, all suggest that oxidation would proceed more slowly than in a relatively favored location.

As the water table fluctuates with the supply of moisture and the physiographic events, the pyritic fuel of the heat source may "burn" faster, slower, or even be quenched. The presence of the primary sulfide zone well above the water table may mean that this part of the section is less permeable than where the oxidized zone gives way to the sulfides at water level, or it may only reflect the former presence of a barricaded high water table, now drained. The uncertainty in attempting to appraise such possibilities is large and it

seems best to point them out merely as qualifying the conclusions reached by straightforward calculation.

RATE OF OXIDATION.

The rate of oxidation of the pyrite has been calculated from the data for holes 9 and 11. The geothermal gradient that can be ascribed to oxidation is about 0.6° F per 100 feet in hole 9 and somewhat less in hole 11. If the present gradient is used to estimate the influence of oxidation in hole 11, the inflection at the water table indicates an oxidation gradient of a little less than 0.6° F; if the "1880 gradient?" shown in Fig. 2 is used instead, the oxidation gradient would be about 0.5° F. The sulfide present is almost entirely pyrite. In the sulfide zone above the water level, pyrite averages 4.91 percent in hole 9 and 3.58 percent in hole 11, according to information supplied by Schwartz. In the sulfide zone lying above the water level in hole 9 (105 feet or 32.0 m) there should be approximately 393 gms (78.6 cc) of pyrite in each column corresponding to a square cm of horizontal section. On this basis, and using the conductivity of 0.008 determined by Birch, an average measured density of 2.50, and an oxidation gradient of 0.6° F per 100 feet, the time required for complete oxidation of the pyrite is calculated as 40,000 years in round numbers. For hole 11, where the sulfide present is less (382 gms in 140 feet) and the oxidation gradient is similar, the data give a figure of about 47,500 years if the "1880 gradient?" of Fig. 2 is used as a base; if the inflection in the present gradient is used uncorrected the calculated time is 41,000 years.

The determination of the depth to the sulfide zone is believed by Schwartz to be accurate within a few feet, and the errors in the thermal constants used are probably small, but nevertheless it is best to regard the figures calculated for the rate of oxidation as only good approximations. Furthermore, they represent the rate under conditions in the immediate geologic past and might change perceptibly with time. With due regard for the uncertainties involved, the results for holes 9 and 11 are believed to be acceptably consistent. As hole 9 has nearly 50 weight percent more sulfide than hole 11, and the gradient has a sharp inflection just above the sulfides, the oxidation gradient can be measured with more confidence and so the writer believes the figure of 40,000 years for complete oxidation of pyrite in this district is the best value to use.

It was pointed out earlier that if all the oxygen used in the oxidation of pyrite were supplied by the air dissolved in rainwater, some 91 liters would be required to oxidize one gram at 50° F. If we assume that approximately 100 liters are needed at 70° F, it is easily seen that the column of pyrite above water level under each square centimeter of surface, which contains about 400 grams of pyrite near hole 9, would require 40,000 liters of air-saturated water to change the sulfide to oxide. The rainfall may be slightly more than 10 inches (25 cm) per year, but it is optimistic to assume that any such quantity as this soaks down through the bedrock to reach the water table. If we do assume such a supply, however, it is apparent that the water needed for complete oxidation would require (40,000 ÷ .025) years or 1,600,000 years.

Thus the present rate of oxidation is about 40 times as fast as that to be expected if it were all due to air trapped in rainwater. It seems logical to assume that even if the rainfall had been twice as great in the past, more than 95 percent of the oxygen fixed in the limonite was supplied by air, pumped into the voids by changing barometric pressure. This conclusion does not mean that the writer believes water unimportant in oxidation; there is ample evidence that where rock is moist it will oxidize more rapidly than where it is dry, but the oxygen carried by a film of water may be renewed over and over again from the air far below the surface, as sulfide withdraws the dissolved gas during oxidation.

If all conditions governing oxidation were identical with those in the ground tested by hole 9, except for the amount of sulfide present, the geothermal gradient should reflect this difference accurately. If, for instance, the equivalent of a layer of pyrite 7.86 meters thick were present and *sufficient oxygen were available,* the oxidation gradient would be ten times as steep and the geothermal gradient just above the sulfide zone would then be equal to the normal gradient plus $10 \times 0.6°$ per 100 feet. However, the amount of heat generated depends as much on the availability of oxygen as of sulfide. A gradient just as steep might be generated by a much thinner but more rapidly oxidizing layer if the permeability were greater, or other conditions more favorable to efficient oxidation existed.

Many years ago, W. H. Emmons studied the problem of the heat generated during the oxidation of sulfide by relating the iron sulfate content of mine water to the exothermic reactions involved.[11] He concluded that oxidation above the secondary sulfide zone generates enough heat to raise the temperature of the ground water about 25° F above that appropriate to an environment of barren rocks at the same depth. This is much more than the temperatures found in the San Manuel district but is less than the temperatures found by the writer in the Tintic district, Utah, in pyritized quartz latite well away from the nearest mine openings.

It is common experience that sulfide ores, when disturbed by mining, oxidize fast enough to generate heat in an impressive way, causing difficult problems for the ventilation engineer. The electric currents set up by undisturbed oxidizing sulfides have been used in the self-potential method since 1912 to aid in the discovery of ore, but the heat that must accompany this oxidation has not been sufficiently considered in the past, and in places may be as useful in locating an ore body as are the galvanic currents.

Measurements in mines in the Tintic district and at Superior, Arizona, show that pyritic sulfide veins commonly are marked by thermal highs from 10° to 40° F above the normal rock temperature, with horizontal gradients of several degrees per 100 feet near them. At many places where measurements were made the increase in rock temperature was perceptible 300 to 500 feet away from vertical veins.

It is possible to take rock temperatures with a mercury thermometer in a mine in a few minutes but if drill holes are to be logged for temperatures a

[11] Emmons, W. H.: On temperatures that obtain in zones of chalcocitization. ECON. GEOL., Vol. 10, pp. 151–160, 1915.

much more rapid and sensitive method should be used than the present maximum thermometer technique. The results in the San Manuel area with the thermometer method suggest the desirability of carrying thermal investigations further with better equipment.

CALCULATIONS.

Conductivity.—

$$Q = \frac{k(\theta_1 - \theta_2)td^2}{x}, \tag{1.0}$$

where

Q = quantity of heat in gm cal
k = thermal conductivity in cal per sec
θ_1 = temperature at x_1
θ_2 = temperature at x_2
t = time in seconds
d^2 = area of cross section
x = distance between x_1 and x_2

If a perfectly insulated bar has its two ends x_0 and x_2 maintained at different temperatures, is of unit cross section, has a conductivity of k_1 between x_0 and x_1, and a conductivity of k_2 between x_1 and x_2, the same quantity of heat must pass through every section of the bar in unit time:

$$Q = \frac{k_1(\theta_0 - \theta_1)}{x_1 - x_0} = \frac{k_2(\theta_1 - \theta_2)}{x_2 - x_1} \tag{1.1}$$

and θ_1, the temperature at x_1, is given by

$$\theta_1 = \frac{\theta_0 k_1(x_2 - x_1) + \theta_2 k_2(x_1 - x_0)}{k_1(x_2 - x_1) + k_2(x_1 - x_0)}. \tag{2.0}$$

If m is the thermal gradient

$$m_1 = \frac{(\theta_0 - \theta_1)}{x_1 - x_0} \quad \text{and} \quad m_2 = \frac{(\theta_2 - \theta_1)}{x_2 - x_1};$$

but $m_1 \neq m_2$ if $k_1 \neq k_2$.

If a substance contains a constituent of different conductivity disseminated through it, the conductivity of the mixture may be closely approximated by assuming the material to be made up of two layers whose thickness is proportional to the volume of the two constituents present. The temperature θ_1 at the assumed interface may be calculated by (2.0), and since the quantity of heat transmitted is the same at every cross section, the overall conductivity k can easily be found:

$$Q = \frac{k_1(\theta_0 - \theta_1)}{x_1 - x_0} = \frac{k(\theta_0 - \theta_2)}{x_2 - x_0},$$

$$k = \frac{k_1(\theta_0 - \theta_1)(x_2 - x_0)}{(\theta_0 - \theta_2)(x_1 - x_0)}. \tag{2.1}$$

Effect of Climatic Changes on Geothermal Gradient.—The general equation for an infinite solid with a known initial temperature distribution and heat flowing only in the x direction is given below.[12]

$$\theta_{x,t} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} f(x + 2h\beta\sqrt{t}) e^{-\beta^2} d\beta, \qquad (3.0)$$

where $\theta_{x,t}$ is the temperature at the point x at the time t in the infinite solid whose diffusivity is h^2 and whose initial temperature $\theta_{t=0}$ at the time $t = 0$ was a function of x, and $f(x) = f(\gamma)$, and γ (the variable of integration) is equal to $x + 2h\sqrt{t}\beta$, and β, the exponent of e, is a constant determined by boundary conditions. It is permissible to split equation (3.0) into several integrals, each of which covers a portion of the space between $-\infty$ and $+\infty$, provided the entire space is represented by the sum of the several integrals. This operation is used when the initial distribution of temperature is represented by different functions of x in different portions of the infinite solid, as, for example, the temperature distribution shown in Fig. 3.

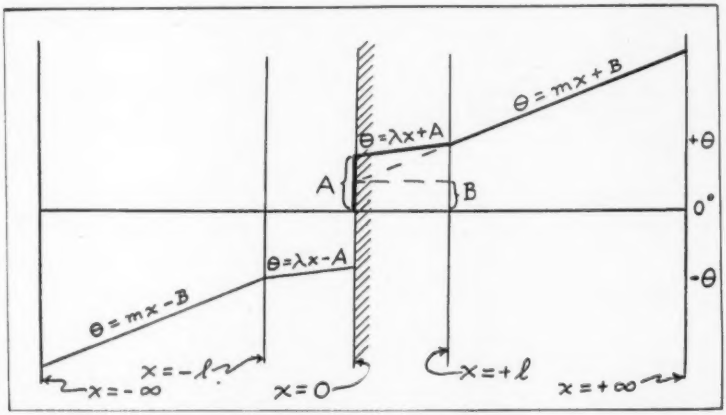

FIG. 3. Initial temperature distribution that will maintain surface temperature (at $x = 0$) constant and equal to drop of A degrees, while gradients readjust to this condition.

We may break equation (3.0) into four parts corresponding to the initial temperature distribution shown in Fig. 3. Let

$$a = \frac{l - x}{2h\sqrt{t}}, \qquad b = \frac{x}{2h\sqrt{t}}, \qquad c = \frac{l + x}{2h\sqrt{t}},$$

and let θ have the values shown in Fig. 3. Then $f(x + 2h\beta\sqrt{t})$ is specified

[12] Ingersoll, L. R., and Zobel, O. J.: An Introduction to the Mathematical Theory of Heat Conduction. Ginn and Company, p. 70, 1913.

from Fig. 3, and (3.0) may be written as:

$$\theta_{xt} = \frac{1}{\sqrt{\pi}}\left\{ \int_{-\infty}^{-c} [m(\beta 2h\sqrt{t} + x) - B]e^{-\beta^2}d\beta + \int_{-c}^{-b} [\lambda(\beta 2h\sqrt{t} + x) - A]e^{-\beta^2}d\beta + \int_{-b}^{+a} [\lambda(\beta 2h\sqrt{t} + x) + A]e^{-\beta^2}d\beta + \int_{+a}^{+\infty} [m(\beta 2h\sqrt{t} + x) + B]e^{-\beta^2}d\beta. \quad (3.1)$$

Equation (3.1) may be transformed into a more usable expression by expanding the terms and removing from the integrals those terms that are constants (or may be so regarded for each valuation of the integral) and integrating the terms that cannot be transformed into the probability integral I,

$$I(\beta) = \frac{2}{\sqrt{\pi}}\int_0^{\beta} e^{-\beta^2}d\beta$$

for which tabulated values are readily available.[13] Performing the operations indicated above and remembering that $I(-\beta) = -I(\beta)$, equation (3.1) may be written:

$$\theta_{xt} = \frac{mx}{2}[I(\infty) - I(c)] - \frac{B}{2}[I(\infty) - I(c)] - \frac{mh\sqrt{t}}{\sqrt{\pi}}[e^{-c^2} - e^{-\infty^2}] + \frac{\lambda x - A}{2}[I(c) - I(b)] - \frac{\lambda h\sqrt{t}}{\sqrt{\pi}}[e^{-b^2} - e^{-c^2}] + \frac{\lambda x + A}{2}[I(a) + I(b)] - \frac{\lambda h\sqrt{t}}{\sqrt{\pi}}[e^{-a^2} - e^{-b^2}] + \frac{mx + B}{2}[I(\infty) - I(a)] - \frac{mh\sqrt{t}}{\sqrt{\pi}}[e^{-\infty^2} - e^{-a^2}].$$

As $I(\infty)$ is 1, and $e^{-\infty}$ is 0, this expression may be written more simply as:

$$\theta_{xt} = mx + \tfrac{1}{2}\left\{ A[I(a) + 2I(b) - I(c)] + B[I(c) - I(a)] + (\lambda x - mx)[I(a) + I(c)] + h\sqrt{t}(\lambda - m)\frac{2}{\sqrt{\pi}}[e^{-c^2} - e^{-a^2}] \right\}. \quad (3.2)$$

[13] Tables of the probability integral and of $\frac{2}{\sqrt{\pi}}e^{-x^2}$, the two functions used in calculating equations (3.2), are available in one volume: Lowan, A. N. Tables of probability functions, Vol. 1; W. P. A. Rept. Project No. 65-2-97-33, Nat. Bur. Standards, 1941.

Where there is a straight line gradient from $x = 0$ to $x = \infty$ and $\therefore \lambda x = mx$, $B = 0$, and $l = 0$, equation (3.2) reduces to

$$\theta_{xt} = mx + A[I(b)]. \tag{3.3}$$

Equation (3.3) was used to ascertain the "1880 gradient?" of Fig. 2. Equation (3.2) was used to calculate the present position and magnitude of the heat wave generated during the Great Drought of 1570 to 1600 A.D.; assuming that the gradient in 1600 was such that $\lambda = 0$, $m = 1.833 \times 10^{-4}$ deg. C cm^{-1} (1° F per hundred feet), $l = 90$ meters, $A = 1.65$, and $B = 0$, the following data were calculated for the gradient in 1944:

Feet	Meters	mx (° C)	Calculated Temp. θ_x	$\theta_x - mx$ (° C)
295	90.00	1.6500	1.6526	.0026
700	213.00	3.9109	3.9364	.0204
800	243.84	4.4696	4.5000	.0304
861	262.47	4.8111	4.8350	.0239
900	274.32	5.0282	5.0465	.0183
1100	335.28	6.1457	6.1628	.0171
1500	457.70	8.3804		.0100

Oxidation of Pyrite.—Many complex reactions may take place during the oxidation of pyrite, but if we assume that ultimately all the iron combined as sulfide changes to ferric hydroxide, the oxidation of pyrite may be written as:

$$2FeS_2 + 15O + (n + 7)H_2O = 2Fe(OH)_3 + 4H_2SO_4 + nH_2O$$

and $2Q$, the heat liberated in this reaction, can be calculated from the corresponding heats of formation:[14]

$$2(35{,}000) + 15(0) + 7(68{,}390) + 2Q = 2(197{,}370) + 4(210{,}300)$$

and $Q = 343{,}605$ gm cal per mol.

Since one gm mol of pyrite is 119.96 gms, the complete oxidation of 1 gm of pyrite yields 2,864 gm cal of heat.

2 mols of pyrite (239.92 gms) require 15 mols of oxygen (240 gms) or a gm of oxygen for a gm of pyrite. Water at 10° C in equilibrium with air at 760 mm pressure contains approximately 0.011 gm (8 cc) of dissolved oxygen per liter; 90.9 liters would therefore be required to dissolve one gm of oxygen.

Rate of Oxidation in the San Manuel District.—The oxidation gradient m in hole 9 is approximately 0.6° F per 100 feet and can be used to compute the heat generated by the sulfides above the water table; this sulfide zone is 105 feet (3,201 cm) thick and contains 4.91 weight percent pyrite.

$$M = \frac{0.6° \text{ F}}{100 \text{ ft}} = \frac{1.09° \text{ C}}{100 \text{ m}}, \text{ or in round numbers } M = 1.1 \times 10^{-4},$$

[14] Data from Handbook of Physics and Chemistry, Twenty-seventh edition, 1942–1944. Chemical Rubber Pub. Co., Cleveland, Ohio.

where the thickness is measured in cm.

$$Q = Mkt = 1.1 \times 10^{-4} \times (8 \times 10^{-3}) \times 31{,}557{,}600 = 27.7707 \text{ gm cal per year per sq cm.}$$

The weight of the column of oxidizing pyrite under each square cm of horizontal area is the weight percent of pyrite times the weight of the rock column in the sulfide zone above water, or $0.0491 \times 2.5 \times 3{,}201 = 393$.

Complete oxidation should release $393 \times 2{,}864$ cal or 1,125,555 cal per sq cm. If this is divided by the heat generated yearly from oxidation (27.771) the time for completion is calculated to be about 40,000 years (40,530). A similar calculation for hole 11, where the thickness is 4,268 cm and the percent of pyrite is 3.58, gives a value of about 47,500 years (47,565) if $M = .91$ (0.5° F per 100 feet), and 41,000 years (41,007) if M is 1.07 (0.59° F per 100 feet).

A general figure more convenient for use may be obtained by assuming slightly different conditions: if the thickness of the pyritic layer is 1 meter and it takes 100,000 years for complete oxidation of the pyrite, then the gradient in material whose conductivity is 0.005 is given by:

$$M = \frac{Q}{kt} = \frac{2{,}864 \times 5 \times 100}{0.005 \times 10^5 \times 31{,}557{,}600}$$

and $M = 9.07 \times 10^{-5}$ or a gradient of 9° C per 1,000 meters (approximately 0.5° F per 100 feet). If the time for complete oxidation was 10,000 years the gradient would be 90° per kilometer (4.94° F per 100 feet) if $k = 0.005$, and would be 45° per kilometer if $k = 0.010$.

EUREKA, UTAH,
Nov. 18, 1947.

REPLACEMENT OF CALCITE BY ATACAMITE IN COPPER CHLORIDE SOLUTIONS.

R. M. GARRELS AND L. O. STINE.

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ABSTRACT.

Replacement of calcite by basic copper chloride has been studied as a function of time, temperature, and concentration in flowing solutions. The replacement does not follow the laws of chemical equivalence; instead, the control is a rough type of catalysis on the calcite surface. The mechanism gives great promise of producing volume for volume replacements.

INTRODUCTION.

In June of 1946, a piece of calcite was dropped in a concentrated solution of copper chloride. By September, 1946, a thick coating of a powdery green material had formed on the surface of the calcite fragment. This was the starting point for an investigation of the replacement of calcite in cupric chloride solutions. The reaction apparently had all the necessary characteristics for easy investigation: it occurred at a rate satisfactory for laboratory studies; a colored product was formed so that the reaction could be followed easily by eye; the system was one similar to types postulated in the replacement of limestones in the zone of oxidation by descending copper-bearing waters; and this natural system could be simulated without troubling about reducing conditions, high pressures, or high temperatures, which accompany so many other geological processes.

In order to obtain quantitative data on the separate effects of temperature, time, and concentration of the reacting solution, arrangement was made for controlled conditions, so that any one of the variables could be changed at will. A series of runs was made, holding everything constant except the factor under investigation. It was hoped, in the beginning, that the effects

of the three controls investigated could be integrated into a single equation, but unforeseen complications have made this impossible.

PREPARATION OF MATERIALS AND EXPERIMENTAL PROCEDURE.

Preparation of Calcite and Replacing Solutions.—The material selected for replacement was uniform rhombs of optical calcite. The specimens were freshly cleaved just before they were to be replaced. In order to assure the greatest possible uniformity, all specimens were taken from a single large rhomb. The fragments averaged about 4 millimeters on an edge, and weighed about 60 milligrams, with a maximum range in weight from 45 to 100 milligrams. No special treatment of the surface of these small rhombs was necessary; checks were made by preparing them in several different ways. In each case, whether they were cleaned in acid, or washed in acetone, or used fresh, the results checked within the limit of experimental error.

The solutions were made up from C. P. cupric chloride ($CuCl_2.2H_2O$) dissolved in distilled water. No special precautions were taken to assure that the water was free from dissolved oxygen or carbon dioxide.

Procedure.—After the calcite rhombs were cleaved, they were weighed (± 0.05 milligram), and suspended by a corner from a strand of human hair. A tiny drop of glue was used to attach the hair. The replacing solution was put into a simple convection heating apparatus.[1] After the solution had been brought to the required temperature, the calcite was suspended in the slowly circulating solution. In all experiments the solution moved past the calcite a constant rate of approximately 0.3 centimeter per second. The temperatures in the apparatus were controlled to 0.5° C.: most runs actually varied less than 0.2° C.

The relatively small size of the specimens used assured homogeneity of material and also made it possible to consider the concentration of the reacting solution constant, because the amount of copper chloride used up by reaction with the calcite was negligible (less than 0.1%) in relation to the total amount in solution. Also, the amount of calcite used up was small (less than 5%) in relation to the total weight of the sample so that the surface area of calcite exposed could be considered constant. The slow constant rate of flow removed the necessity of considering local changes in concentration as the reacting solution was used up. After the specimen had run for the desired length of time, it was removed from the solution, dried, and placed in a concentrated ammonium hydroxide solution, which stripped the fine-grained green film formed by the reaction from the calcite surface. After stripping, the specimen was washed, dried, and weighed again. Samples of unreplaced calcite dropped in the ammonium hydroxide for the same length of time showed no loss in weight, so it was assumed that all loss in the ammonium hydroxide solution represented copper compounds formed by reaction with the calcite in the replacing solution.

The maximum error in the experimental procedure came in the weighings; although the balance used was accurate to 0.05 milligram, the amount of

[1] Garrels, R. M., Jones, C. L., and Howland, A. L., Apparatus for studying crystal formation: Science, vol. 105, p. 46, 1947.

material formed in the reaction at low concentrations, low temperatures, and over short time intervals was of the order of 1 milligram. Consequently a maximum experimental error of 5 to 10% was expected.

DISCUSSION OF EXPERIMENTAL RESULTS.

General.—For a considerable time after the beginning of the experiments it was believed that the green material formed by the reaction was malachite, and that the reaction probably could be written:

$$2\ CuCl_2 + CaCO_3 + 2\ H_2O \rightarrow Cu_2(OH)_2CO_3 + CaCl_2 + 2\ HCl. \quad (1)$$

However, X-ray analysis of the product showed that it was atacamite, $Cu_4(OH)_6Cl_2$. A balanced reaction for the formation of atacamite can be written:

$$3CaCO_3 + 4\ CuCl_2 + 6\ H_2O \rightarrow 3\ CaCl_2 + 3\ H_2CO_3 + Cu_4(OH)_6Cl_2. \quad (2)$$

A consideration of the ionic equilibria involved indicates, however, that such a reaction does not occur. If the various ionizations are set up, and the interactions which must take place shown, it becomes apparent that there is no reason to expect that equivalent quantities of materials should be formed:

$$\begin{array}{lcl} 4CuCl_2 & \leftrightarrows & 4Cu^{++} + 2Cl^- \leftrightarrows Cu_4(OH)_6Cl_2 \\ & & + \quad + \ 6Cl^- \\ 6H_2O & \leftrightarrows & 6OH^- + 6H^+ \\ & & \quad + \\ 3CaCO_3 & \leftrightarrows & 3Ca^{++} + 3CO_3^= \\ & & \quad \downarrow\uparrow \\ & & 3H_2CO_3 \leftrightarrows 3H_2O + 3CO_2 \end{array} \quad (3)$$

The process consists of two interrelated but separate reactions. The formation of the atacamite could not proceed without the formation of the carbonate ion, but it need not form quantities of atacamite equivalent to the amount of calcium carbonate dissolved. Consequently, the mechanism of the reaction is essentially as follows: at the surface of the calcite, the hydrogen ion from the solution (controlled by the hydrolysis of the $CuCl_2$) is tied up by the carbonate ion of the calcite. Therefore, at the surface, there is a high local concentration of hydroxyl ion. This hydroxyl, in contact with the copper ions and the chloride ions, is sufficient to exceed the solubility product of atacamite, which precipitates at the surface of the calcite. At the concentrations of copper chloride which were used in the experiments, the pH was sufficiently low for enough carbonic acid to be formed to release carbon dioxide, and for the calcite to be dissolved. There probably is no necessity for this to happen; atacamite might be formed continually in a flowing solution at a calcite surface, even though the pH were too high to have carbon dioxide released. It is the "holding" action of the carbonate ion on the hydrogen ion which is of primary importance.

Malachite was not obtained in any of the experiments, although it is easily synthesized by mixing copper chloride solution with sodium carbonate or sodium bicarbonate *solution;* in that case the carbonate ion concentration at the site of reaction is very high, and the reaction is forced to malachite rather than atacamite. On the other hand, when the source of carbonate ions is the *solid* calcium carbonate, the carbonate ions are tied up effectively

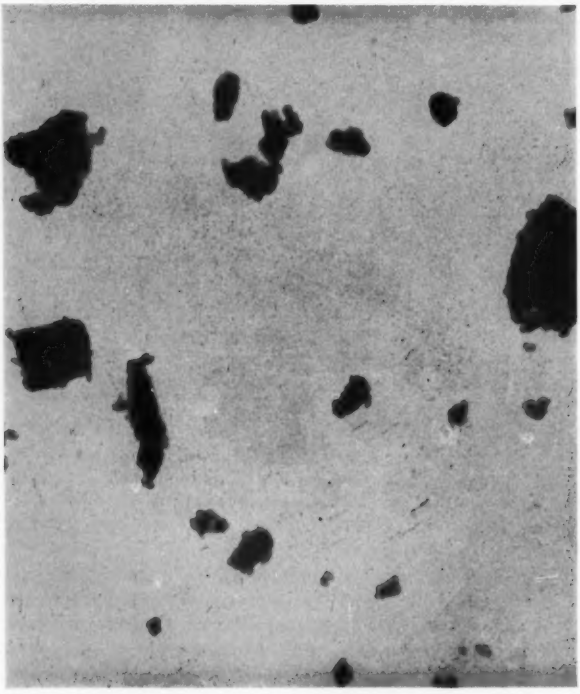

FIG. 1. Electron photomicrograph of atacamite. Magnification 27,400 ×.

by the hydrogen ions, and maintained at such a low concentration that malachite cannot form. The solubility product of malachite was not determined, and consequently the limiting conditions for the formation of one or the other of the two copper salts have not been determined.

Nature of the Atacamite Films Formed by Replacement.—The coating of atacamite which forms on the calcite is light green, extremely fine-grained, and surprisingly adherent. None of the films formed in this study was more than a fraction of a millimeter thick, but as far as could be determined, the original outline of the calcite rhombs was preserved. One electron microscope photograph picture was taken on the material of the film (Fig. 1), and

shows that the particles are discrete, crystalline, and have a diameter measured at most in a few microns. The film from which the material was selected was several days old at the time of the photograph; at present, no evidence has been gathered to determine the effect of aging on the original material, or whether there is a wide size range of material depending upon the concentration of the solution used, or the temperature at which the replacement was made. However, none of the material was coarse enough to show individual grains under a 500 × magnification with a petrographic microscope.

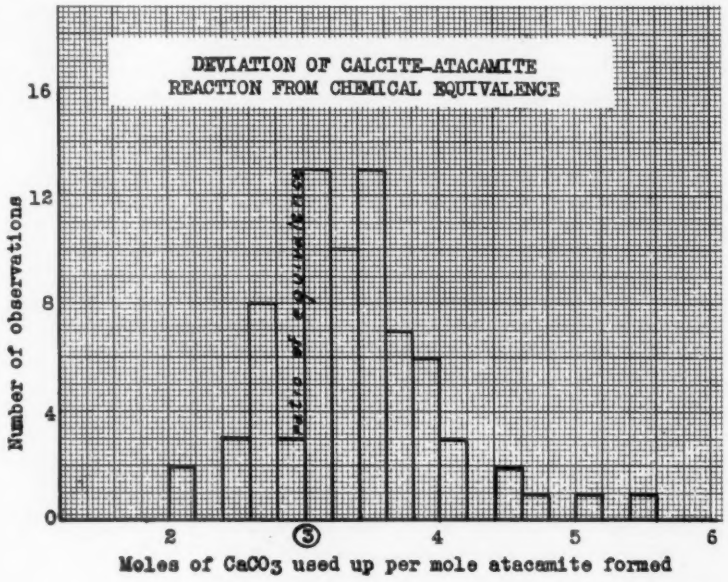

FIG. 2.

Quantitative Results of the Study.—A series of graphs has been prepared of the results of the replacement studies, showing the effects of time, temperature, and concentration on the formation of atacamite and the solution of calcite. Figure 2 demonstrates that the formation of atacamite cannot be accounted for by a straightforward chemical reaction; when the ratio of atacamite formed to calcite used up is plotted for all the experiments, there is a wide divergence, both greater and smaller, from the expected 3 to 1 ratio of the balanced chemical reaction (equation 2). It is easy to explain those data which indicate that less atacamite was retained at the surface of the calcite than is required by the reaction—a fair amount of material can be expected to slough off the calcite surface as colloidal loss—but a number

of runs show that the amount of atacamite formed is in excess of the amount which should be formed. Furthermore, the excess is far too great to be explained by experimental error. It is these runs that show retention in excess of the amount to be expected from a balanced chemical reaction which substantiate the explanation of atacamite formation advanced in equation 3.

It was very difficult to find a satisfactory basis for expressing the rate of replacement of the calcite by the atacamite. First an attempt was made to express it by plotting the amount of $CaCO_3$ used up per unit area of calcite surface as a function of the other variables, assuming that the $CaCO_3$ used was

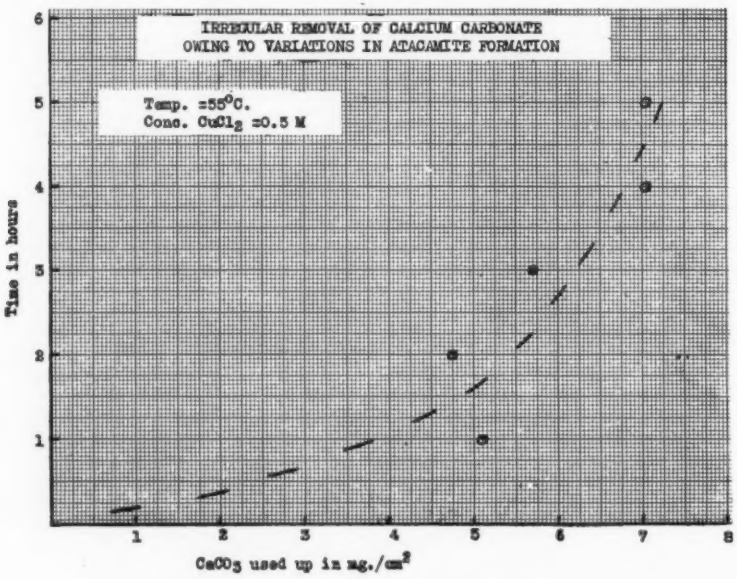

FIG. 3.

equivalent to the atacamite formed. Figure 3 is plotted on this basis, and the spread of the data is so great that the curve which has been drawn is highly unreliable. All the reasons for the spread are not known; most of the variations undoubtedly are due to differences in colloidal loss. Finally a satisfactory but somewhat complicated method was hit upon. In Figs. 4, 5 and 6, the replacement of the calcite is shown by plotting the amount of calcite used up per unit of surface area against the other variables, and then comparing only those data in which the molecular ratio of atacamite formed to calcite used up was constant. When this is done, a family of curves can be drawn, which show the varying rates at which the calcite is used up depending upon how much protecting film of atacamite is formed. In Fig. 4, which shows the effect of time, a family of logarithmic curves results, the rate of replace-

ment slowing as the film thickens. This corresponds perfectly to the result to be expected from diffusion through a porous film. Note that for films which show lower and lower retention of atacamite, the rate of solution of the calcite increases toward the inevitable linear rate which would result if all the atacamite which was formed were sloughed off immediately. Figure 5 shows the effect of concentration, which is closely comparable to the effect of time. In other words, the effect of an increase in concentration would be to increase the rate of reaction linearly, if there were no protecting film. Figure 6 shows the effect of increase in temperature on the replacement rate.

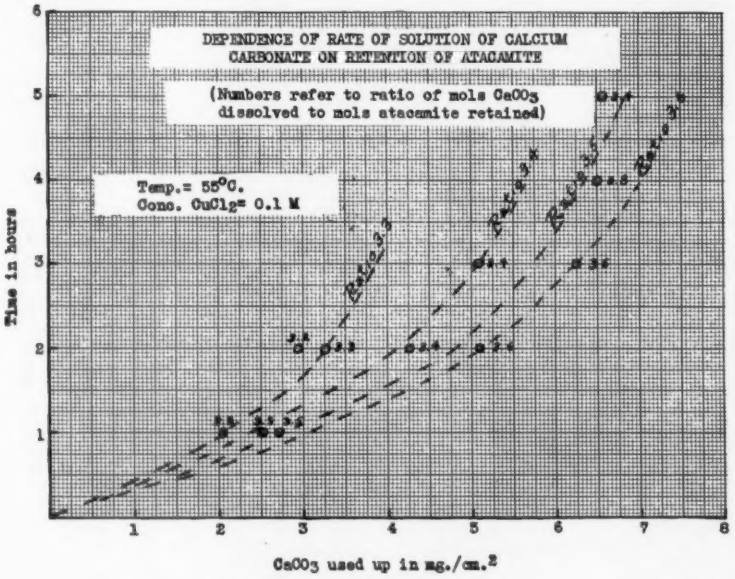
DEPENDENCE OF RATE OF SOLUTION OF CALCIUM CARBONATE ON RETENTION OF ATACAMITE
(Numbers refer to ratio of mols CaCO3 dissolved to mols atacamite retained)
Temp.= 55°C.
Conc. CuCl2= 0.1 M
Time in hours
CaCO3 used up in mg./cm.2

FIG. 4.

This graph is the least satisfactory of the three; the spread of the data is very great, even when equal retention ratios are compared. The curve as drawn expresses the overall data fairly well—it also fits the result to be expected from theory—the rate of the reaction is increased logarithmically with increase in temperature; thus the effect of the temperature increase alone would be to use up the calcite at a logarithmically increasing rate. This is balanced by the logarithmic slowing of the rate of solution of calcite as the covering film of atacamite thickens, so that the overall effect is to give a linear rate of replacement.

There is perhaps some question as to whether the rate of formation of the atacamite film will not be much slower or faster depending on the particular crystal face which has been exposed to the solution. In the experiments this

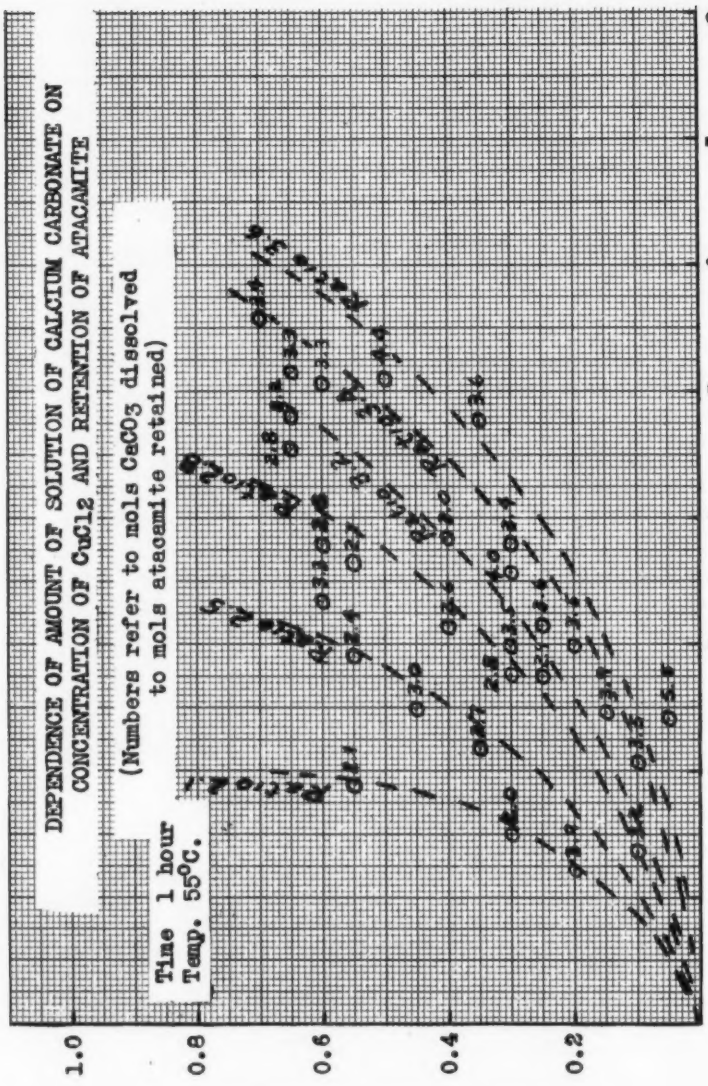
DEPENDENCE OF AMOUNT OF SOLUTION OF CALCIUM CARBONATE ON CONCENTRATION OF CaCl2 AND RETENTION OF ATACAMITE
(Numbers refer to mols CaCO3 dissolved to mols atacamite retained)
Time 1 hour
Temp. 55°C.
Concentration in mols per liter
1.0
0.8
0.6
0.4
0.2
1
2
3
4
5
6
7
8
CaCO3 used up in mg./cm.2

FIG. 5.

factor was eliminated as far as possible by using only rhombohedron faces, and in exposing them in exactly the same way every time. There was no noticeable difference in the thickness of the replacing film on the faces exposed to direct flow as contrasted to those in the lee of movement. The formation of atacamite probably is a function of the reticular density of the carbonate ions at the particular face that is exposed; a few preliminary experiments on faces other than the rhomb indicates that the rate of replacement is of the same order of magnitude, as might well be expected.

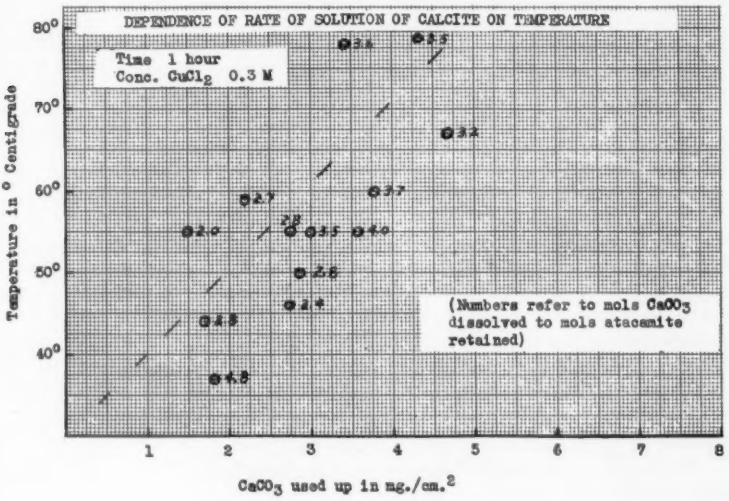

FIG. 6.

SOME GEOLOGIC IMPLICATIONS OF THE ATACAMITE REPLACEMENT MECHANISM.

Although atacamite is a relatively rare mineral in nature, the control of the deposition by local conditions at the surface of the calcite has rather interesting possibilities in terms of controls of mineral deposition of many kinds. The calcite acts as a kind of solid "buffer," causing the deposition of a mineral at its surface which would normally be soluble in the moving solution. Furthermore, the effect is extremely local, and the replacing material is very fine-grained. All these features have a very striking resemblance to the kind of mechanism which is needed for metasomatic replacement. If, for instance, a limestone were replaced, instead of a single calcite grain, the solution of each grain would be followed by the deposition, micron for micron, of atacamite. There is every reason to expect that the textures of the original limestone would be preserved to a very high degree. Studies of grain aggregates are now in progress.

FEB 26 1949

Some criticism may accrue to us, because chloride solutions were used instead of the sulphate solutions which are so much more common in ground water replacements in nature. However, it might be remarked here that tentative experiments in copper sulphate solution resulted in the formation of basic copper sulphate (exact form undetermined) at the surface of the calcite in a reaction which is apparently a strict analogue of that by which atacamite is formed. Although in attempts to expedite the laboratory work concentrations were used which are much higher than those in nature, it is not by any means certain that scaling the concentration down will result in a change in the phase which precipitates. We will be very much interested in determining the boundaries of the atacamite-malachite system, and also in examining actual specimens from our collections to see whether they actually are the basic chloride or the basic sulphate.

This is a very small beginning on the whole problem of quantitative control of replacement, but it gives a first glimmer of the possibilities of predicting the characteristics of a limestone which will be most amenable to complete replacement. The logarithmic decrease in replacement rate with time and concentration as the thickness of the replacing film increased serves to emphasize the difficulties in replacing rocks with coarsely crystalline grains. For instance, it will take much more than twice as long to replace a limestone with grains 1 millimeter in diameter as it will one with grains 0.5 millimeter in diameter, granting the same rate of flow of replacing solution through them. Replacement rate studies obviously must be coupled with permeability studies before predictions can be made, but the work presented gives some data on the controls for any individual grain.

ACKNOWLEDGMENT.

This work was carried on as a result of a grant from the Graduate School of Northwestern University.

NORTHWESTERN UNIVERSITY,
EVANSTON, ILL.,
November 3, 1947.

THE MUZO EMERALD ZONE, COLOMBIA, S. A.

VICTOR OPPENHEIM.

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ABSTRACT.

The Muzo Emerald Mines represent the only large emerald deposits that can be successfully mined and that produce the highest quality emeralds known. Although mined in a very primitive way for the last 400 years, Muzo still has quite unpredictable emerald reserves, which do not seem to have diminished after centuries of mining. The invariable relation of the Muzo emeralds with the Cretaceous Villeta shales is quite peculiar and has not yet been given an adequate explanation.

INTRODUCTION.

THE emerald zone of Muzo is situated in the valley of Río Itoco, tributary of the Río Minero or upper Río Carare. The mines are located at about 100 km. north of Bogotá, at an elevation of about 600 meters above sea level, and can be reached from Bogotá by railroad or highway to the town of Chiquinquirá, then by highway to the village of Muzo; the Muzo mines in the Government reserve zone are at about 8 km. from the village by mule trail.

The Muzo mines and the surrounding area were visited and investigated by the writer in January of 1947. The mines are presently not in operation but the Government that owns them maintains an administrative staff and police force to protect the Government lands from "pirate" miners; these, however, are numerous, and illegal mining, mainly at night, has always been practiced in the region.

When the Muzo mines together with the Coscuez mines, at a short distance to the north, were in operation, they produced the highest quality emeralds in Colombia, at a rate of about 13,000 carats annually.

The only other important emerald mine in Colombia is the Chivor mine, some 90 km. northeast of Bogotá, in the valley of Río Guavio; this is privately

owned by an American concern but is also not in operation at present. The findings made in the Chivor area, in the region of Somondoco, are sporadically worked by the local inhabitants, mostly illegally, and their output is not known. Other findings of emeralds known in Colombia, such as at the Nemocon salt mines, seem to be of no economic importance.

The only other country in South America where emeralds are known to occur is Brazil, but the findings there are sporadic and do not constitute emerald bearing deposits as in Colombia.

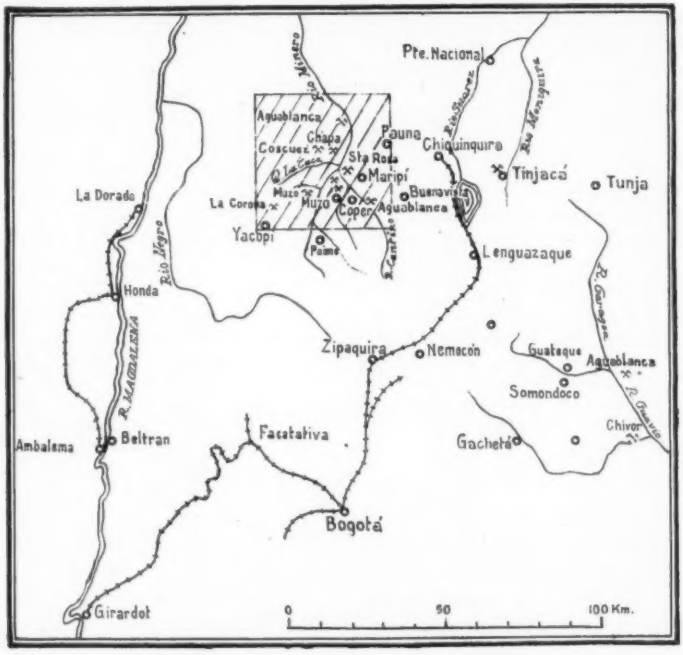

FIG. 1. Muzo Emerald District, Colombia.

Historical Data.—Although emeralds were known and used by the Indians of Colombia long before the arrival of the Spaniards, the tradition of the Muzo emeralds dates since 1539 when the Spaniards first tried to penetrate the Muzo country. The first Spanish expeditions to the Muzo country were unsuccessful and the Spaniards were defeated by the warlike and aggressive Muzo Indians. It was not until 1559 that the hostile Indians were dominated and the settlement known as Santísima Trinidad de los Muzos was founded.

The first emerald beds were discovered in the Cerro Itoco in 1564. They were mined since then intermittently by the Spanish Crown, the Government of the Republic and private enterprises till 1939.

Periodically the exploitation would become intense with the increased value of the gems, turning into a veritable "green fever" in 1904; the production, however, would lag when the value of the stones declined and the accumulated stocks were large, causing a periodical closure of the mines; they would reopen again as soon as the existing stocks were depleted.

Despite the almost four centuries of exploitation, the Muzo emerald deposits have not shown any signs of exhaustion of the emerald bearing formation.

GENERAL GEOLOGY.

General.—The topography of the Muzo region is shaped by the deep valley of the Río Minero and its numerous torrential tributaries and mountain creeks. The terrain is very mountainous and broken, forming steep and abrupt mountain slopes. The soil is fertile and the vegetation is dense and subtropical.

Outside of the village of Muzo, the region is sparsely inhabited; most of the inhabitants are descendants of the Muzo miners. Although formerly the region of Muzo was affected by the yellow fever, this has now been brought under control.

The climate is hot and somewhat moist, but the dry season and the prevailing breezes during that period make living conditions fairly acceptable.

Geologic Formations.—Geologically the formation in which the emeralds are found in the Muzo area is of Lower Cretaceous age, known as Villeta Formation(1).[1] This consists of a great thickness of black shales and limestones. The shales are rich in organic matter and are carbonaceous or bituminous. Their rather abundant fauna of amonites and exogyrae indicates their exact age and marine origin.

In the Muzo area, the Villeta shales are accompanied and traversed by beds and veins of calcite and dolomite which are often associated with nodules and lenticular concretions of pyrite. Veins of albite and barite, as well as quartz and pegmatite bodies, also occur in the area and are associated to some extent with the emerald bearing formations.

The shales and limestones of the Villeta Formation in the Muzo area are intensely folded. The periods of folding are, however, different and affected the formations to a different degree. Faulting, and particularly thrust-faulting, with the associated brecciation have played a highly important role in the mineralization of the Muzo area.

As the presence of pegmatitic dikes in the lower part of the Villeta Formation indicates, with the presence of quartz, feldspar, sericite, apatite and other minerals, the sources of the mineralization were due to deep-seated igneous intrusions, which penetrated the Villeta shales during a Tertiary diastrophism. Having encountered the beds of the Muzo area affected by

[1] Numbers in parentheses refer to Bibliography at end of paper.

faulting and previous diastrophic compressions, the mineralizing solutions and gases penetrated the strata under different conditions in distinct sections of the sedimentary column. Thus in the Muzo area the conditions were accidentally quite peculiar and particularly favorable for the formation of emerald bearing beds and veins.

LOCAL GEOLOGY OF MUZO BEDS.

Within the Villeta Formation of the Muzo area there can be clearly distinguished two geological elements which are known and have been described by several observers (2) as "Cambiado" and "Emerald beds." These two are separated from each other by two characteristic layers known as "Cenicero" and "Cama." The following are the characteristics of each of these elements typical of the emerald bearing area of Muzo:

"Cambiado."—This consists of a great thickness of black shales and limestones, generally folded in steep folds and traversed by numerous veins of calcite, dolomite, with pyrite and quartz; veins of albite are also common. The formation is faulted and fractured.

"Emerald beds."—These invariably overlie the "Cambiado" discordantly. They consist of thin shale beds of a deep black color, alternated with thin calcite and aragonite veins; pockets of black calcite crystals are found in this formation together with pyrite concretions; crystals of dolomite, parisite, albite and emeralds are irregularly disseminated in these beds or in the calcite veins. The "Emerald beds" are intensely folded into small narrow and irregular folds and wrinkles. The unconformity between the "Emerald beds" and the "Cambiado" is occupied by two intermediary elements which, however, occur sporadically and in many places one of them may be missing. These are known as "Cama" and "Cenicero."

"Cama."—This is an agglomeration of fairly large calcite crystals with some crystals of hyaline quartz, the whole cemented with a limestone and quartz binding. The "Cama" invariably overlies the "Cambiado" and in many instances it is connected with the calcite veins, which penetrate through the "Emerald beds" or the "Cambiado" formation.

"Cenicero."—This overlies the "Cama" layer and reaches a thickness of about one meter but is generally very irregular. It appears as an agglomeration of small crystals of calcite, dolomite, quartz and pyrite in a fine limestone cement; a fine black shale dust is characteristically found in the cavities of this layer. Commonly the "Cenicero" is connected with bodies of albite and in some instances it forms veins in the "Emerald beds." In many places the "Cenicero" is preceded by a thin irregular layer of albite which locally replaces the calcite. Barite, in fragments and crystals, is also generally found in the "Cenicero" which is classified by R. Scheibe in two different types: the gray "Cenicero" and the red "Cenicero."

ORIGIN OF THE EMERALDS.

The peculiar geological conditions of the Muzo area are undoubtedly due to complex and exceptional conditions of diastrophism and subsequent min-

eralization, which apparently recurred at different periods with varying intensity and various mineralizing solutions.

J. E. Pogue (3) infers that the emeralds were formed by pneumatolytic mineralization with a general temperature below 575°. The mineralizing solutions penetrated the fault planes and fractures of the sedimentary beds; the lower veins having been filled with calcium carbonate, while the gaseous elements reached the uppermost crevices of the strata, crystallizing into emeralds and the associated minerals. Since apparently the "Emerald beds" of the Muzo area appear overthrusted over the more massive and compact "Cambiado" beds, it seems reasonable that while the latter were penetrated at depth by the igneous magma and its pigmatitic apophyses, the mineralizing solutions filled completely the veins in the "Cambiado," and the lighter gaseous mineralizing vapors penetrated first into the plane of thrusting, forming the crystallization of the "Cama" and "Cenicero" and their gaseous elements then crystallized in the overlying intensely shattered and folded emerald beds. Diastrophic movements, however, continued after the mineralization period was completed and this accounts for the frequent flaws in the emeralds, characteristic of the Muzo crystals.

It must be said that the subject of the origin of emeralds has not been fully studied and to that effect it is interesting to call attention to the frequent relation of the emerald-bearing formations and the salt beds and domes in the Villeta Formation, since not only are the Muzo area emeralds related to salt springs and salt beds, but emeralds were also found in the Nemocon salt beds and the Zipaquirá salt mines, north of Bogotá, all imbedded in the same formation (4).

MINERALOGY.

The emerald, which is a variety of beryl with the peculiar emerald green color, consists chemically, in the case of the Muzo crystals, as analyzed by Boelbling (5), of the following elements which may vary somewhat in different specimens:

SiO_2	61.4
TiO_2	0.8
BeO	9.7
Al_2O_3	24.3
FeO	1.2
	97.4

The Muzo emeralds form hexagonal crystals, normally of a prism in which the height is approximately equal to a side of the base; it has a conchoidal fracture; hardness 7.5 and density 2.65.

The emeralds of the Muzo area occur in pockets or are found imbedded in the calcite veins of the emerald formation or imbedded in the formation proper or sometimes in the "Cenicero." The crystals are mostly small and rarely exceed 2 to 3 centimeters. When extracted the crystals are generally clear and only later exhibit flaws. Most of the crystals are of a green color,

varying however from deep green to almost white; some of them are dark or even black due to inclusions of carbonaceous matter.

The minerals commonly associated with the emeralds in the Muzo area are: calcite, dolomite, parisite, pyrite, and quartz, more rarely barite, fluorite and apatite.

FIG. 2. Emerald bearing calcite vein.

Twin crystals of emeralds, as well as emeralds of peculiar shapes and forms of crystallization, are not uncommon and these have been described by F. Bernauer (5). Unflawed emeralds are rare and large unflawed crystals are unknown.

The peculiar oily green color of the emeralds from the Muzo area makes them exceptionally valuable, as compared with the stones from the Chivor mines and other localities; their value is thus enhanced by their peculiar color and rarity.

MINES IN THE MUZO AREA.

Emeralds were found and mined during different periods in the general area of the Muzo mines since the latter were discovered. These occurrences or old emerald mines are situated within a radius of about 25 km. to the north and east of the Muzo mines proper. Emeralds in these localities occur in formations identical to the ones of Muzo and are associated with the same minerals as the latter.

The following are the mines or localities where substantial amounts of good emeralds are known to have been extracted.

Coscuez Mines.—The emerald-bearing zone of Coscuez consists of about four main mines which are located some 15 km. N.E. of the Muzo mines in the valley of the Río Minero. The Coscuez mines have not been worked for many years; the gems that they produced are, however, famous for their exceptional deep green color and elongated crystals. Salt springs are known to exist in the zone of mines.

La Chapa Mines.—These are located somewhat south of Coscuez in the lower part of the Quebrada Lacaca. Little is known about this mine as it has been abandoned for so many years that even the exact location of its emerald veins is presently unknown.

Tambrias or Peña Blanca Mine.—This mine is located some 25 km. N.E. of Muzo, but as in the case of the La Chapa mine, very little is now known of the emeralds there, as the mine has not been worked for a considerable time.

Camancha Mine.—This is situated near the village of Coper, some 10 km. S.E. of Muzo and near the Camancha salt mines. The emerald bearing veins are there fairly narrow, but numerous, and they have produced considerable amounts of fairly good emeralds.

Alumbral Mine.—This is located in front of the Muzo mine, on the right bank of the Río Minero, and near the mouth of the Quebrada Alumbral. The mine has been discovered only recently on privately owned lands. The emeralds occur associated with barite and albite and the geology of the emerald bearing beds is identical with the Muzo formations. The extracted emeralds are of high quality and similar to those found in the Muzo mines.

Guincha Mines.—In an unpublished report E. Williamson (6) reports on a prospective emerald mine at Guincha situated some 10 km. E.S.E. from Muzo and with geological conditions similar to the Muzo mines; however, it was never worked.

EXPLOITATION METHODS IN MUZO.

None of the Muzo mines, Government or privately owned, have been in exploitation since 1939. Now, however, the Government has leased the National mines to the Bank of the Republic, which has plans to reopen the Muzo and Coscuez mines shortly. When in operation, the Muzo mines were worked rather primitively. The mountain face with emerald beds was first cleared and exposed, then terraces were cut on the slope of the mountain forming a broad amphitheatre; the workmen operated on each terrace following the course of the emerald-bearing veins; the shales and limestone slabs were thrown to the lower part of the mine from where they were carried away by running water. No dynamite was used in these open pit workings since it is very detrimental to the emeralds, which are thus shattered and damaged. The mining was carried out almost totally by means of long bars of 1½ inch round iron, pointed at one end and flattened at the other.

The parts of the veins containing emeralds were picked out by hand and deposited at a sorting office where they were cautiously broken up to smaller fragments and the emeralds were picked out and sorted. The fragments in some of the tailings were washed, not to separate the emeralds whose specific

gravity does not differ from the rest of the material, but in order to pick out the small crystals that remained unnoticed. The emeralds were finally classified by color, transparency, absence of fractures and "gardens" and size. The emeralds of very low quality were usually destroyed.

This method of exploitation was used in Muzo for centuries and although simple and primitive has not been improved as yet.

BOGOTÁ, COLOMBIA,
October 23, 1947.

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SOME SOLUTIONAL FEATURES OF THE LIMESTONE NEAR LEXINGTON, KENTUCKY.

D. K. HAMILTON.

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ABSTRACT.

Field work on the Ordovician limestones and shales of the Lexington area, Kentucky, has shown that no appreciable quantity of ground water is transmitted through interstitial openings in these rocks. Ground-water movement is restricted to joint planes and, to a lesser extent, bedding planes that have been enlarged by solution. Studies of these planes indicate that solution has been effective only to a limited depth below the land surface. The bottom of the solutional zone is an exaggerated replica of the land surface, showing a greater depth of the solutional zone below stream valleys. The greater depth is attributed to the greater accumulation of ground water, the dissolving agent, in those areas. Modifications of the ideal condition are effected by the less soluble beds and the configuration of the land surface.

The underground drainage systems of the area develop in a manner similar to rectilinear stream patterns, showing a definite alignment along the two joint sets of the area. Directional solution has taken place where one of these joint sets has been developed to the exclusion of the other.

PURPOSE OF THE INVESTIGATION.

It is the purpose of this paper to illustrate some of the solutional features affecting the occurrence of ground water near Lexington, Kentucky. The field work and collection of data have been a part of the studies of the Ground Water Division, U. S. Geological Survey, in cooperation with Fayette, Bourbon, Jessamine, and Scott Counties, through the Department of Mines and Minerals of the Commonwealth of Kentucky. Field work was begun in October 1945 and is being carried on as a 3-year study of the ground-water conditions in the above counties (Figs. 1, 3).

ACKNOWLEDGMENTS.

The author is greatly indebted to D. J. Jones, State Geologist of Kentucky, for his advice and criticism of the material contained herein, as well as for his active participation in the collection of data for this paper. Sincere appreciation is due the members of the Department of Geology, University of Kentucky, for their advice and criticism during the progress of the field work.

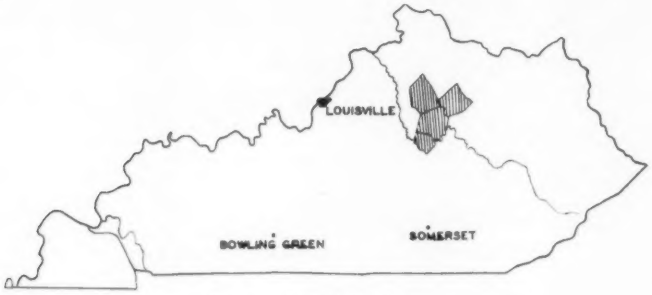

FIG. 1. Location of area.

STRATIGRAPHY.

The exposed formations in this area are sedimentary limestones with interbedded shales and bentonites. The formations are of Lower, Middle, and Upper Ordovician age. They are represented in Fig. 2. A brief description of the strata cropping out in the area follows:

Highbridge Group.

The rocks of this group are the oldest rocks exposed in Kentucky and are questionably correlated with the Chazy and Stones River strata of other areas. It is possible that the Tyrone limestone, the upper unit of the group, is wholly or in part of Trenton age.

Camp Nelson Limestone.—A thickness of not more than about 310 feet of the Camp Nelson limestone is exposed in the area. From 200 to 300 feet of limestone is present in central Kentucky between the lowest exposed Camp Nelson and the Knox dolomite. The Camp Nelson is essentially a lithographic type of limestone, but it contains many recognizable masses of magnesian limestone. As magnesian limestone is typical of the overlying Oregon limestone and lithographic limestone is typical of the Tyrone limestone, the Camp Nelson might be described as a mixture of the types represented by the Tyrone and Oregon limestones.

Oregon Limestones.—The Oregon limestone probably ranges from about 15 to 35 feet in thickness in the area. It is cream to buff in color and in many places shows gray or black banding parallel to the bedding. The Oregon is a finely crystalline magnesian limestone and is quarried for use as road metal.

Tyrone Limestone.—The Tyrone limestone is approximately 90 feet in thickness. It is a very pure limestone of birdseye or, in some places, lithographic type. Three bentonite beds are interlayered with the limestone. The lowermost of these beds is about 1 foot thick and occurs about 10 feet

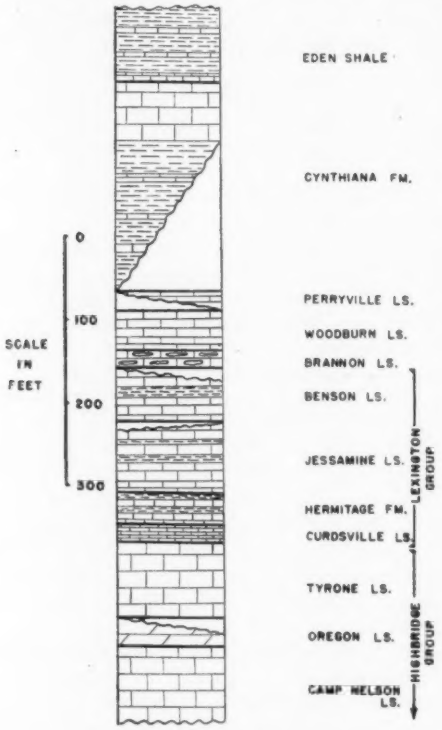

FIG. 2. Stratigraphic section.

above the Tyrone-Oregon contact. The second occurs about 10 to 22 feet below the Tyrone-Curdsville contact and may be a few inches or a few feet in thickness. The third horizon occurs at—and, where present, marks satisfactorily—the contact between the Tyrone and the Curdsville.

Lexington Group.

Curdsville Limestone.—This formation is a cherty, coarsely crystalline gray-blue limestone, about 20 feet in thickness. In other areas, showing thicker sections, a bentonite bed known as the fourth bentonite has been reported 25 to 27 feet above the Curdsville-Tyrone contact.

Hermitage Formation.—This formation is about 35 feet thick and consists of thin-bedded fine-grained gray-blue argillaceous limestone with a considerable amount of interbedded shale.

Jessamine Limestone.—This unit consists of 75 to 80 feet of thin- to medium-bedded gray-blue limestone with thin layers of shale.

Benson Limestone.—This unit ranges in thickness from 35 to 40 feet and consists of coarsely crystalline blue-gray limestone with some shaly partings.

Post-Lexington Rocks.

Brannon Limestone.—This unit is about 15 feet in thickness and consists of finely crystalline siliceous limestone which weathers to a very cherty residue.

Woodburn Limestone.—This unit is about 40 feet thick and consists of coarsely crystalline phosphatic limestone.

Perryville Limestone.—This unit consists of a gray crystalline limestone ranging in thickness from 15 feet to a knife edge, being thinnest or absent along the crest of the Cincinnati arch in Fayette County.

Cynthiana Formation.—This formation includes 40 to 150 feet of limestone and shale. Owing to basal overlap toward the Cincinnati arch, the thinnest sections are present along the crest of the arch.

Eden Shale.—This formation consists of 150 feet of clay shale with a few thin lenses of crystalline limestone.

STRUCTURE.

The area under consideration lies upon the crest of the Cincinnati arch (Fig. 3). From the crest of this arch the rocks dip gently to the east and west at the rate of about 40 feet per mile. This arch has possibly been effective as a paleogeographic element since early Ordovician time. Tertiary uplift has not modified the elements of the arch as a major structural feature in any important way.

Two large fault systems are recognized. The Hickman fault system consists in most of its course of two parallel faults bounding a graben, and numerous complementary cross-faults. It follows roughly the axis of the Cincinnati arch, trending approximately N. 40° E., several miles southeast of the crest of the arch (Fig. 3). The Kentucky River fault system forms either a graben or single fault with the downthrow away from the crest of the arch and passes across the southern portion of the area, extending beyond the limits of investigation with a trend of about N. 80° E. The faults of these systems are of the normal type, and the systems show many cross-faults and local directional changes.

There are two prominent sets of joints in the area. One set trends approximately N. 60° W., the other N. 30° E. The appearance of other sets and deviations from this regional alignment may be attributed to local changes of the regional structure. In the massive, brittle formations such as those of the Highbridge group, the joints show more continuity—in both vertical and linear directions—than do those in the less massive and somewhat less

brittle limestones of the Lexington group. The bentonites and clay shales of the area, the least brittle of all the stratigraphic units, show virtually no jointing. This is attributed to their more plastic nature and to the lack of solutional activity in these beds, so that the existing joints are unobtrusive.

FIG. 3. Major structural features of the area.

CENOZOIC HISTORY.

Successive uplifts during late Tertiary time renewed degradational processes after early Tertiary peneplanation. The major stream of the area, the Kentucky River, has its origin in the Pennsylvanian formations south and east of Lexington and was supplied by those formations with sand. In flowing across the limestones and shales near Lexington, this sand-laden stream cut downward to a depth of 300 to 400 feet below the upland level. The Lexington area remains as a limestone plateau in which subsequent erosional activity has been essentially restricted to solutional processes. The present topographic lows seem to have been localized by two controls. Some of them seem to have been produced entirely by the process of solution, without regard to preexisting topography. The remainder, and majority, seem to have developed along preexisting drainage lines inherited from the Lexington peneplain. Adjustment by the smaller streams has been accomplished only

near their mouths, and they are only slightly incised at distances greater than 2 or 3 miles from the gorge of the Kentucky River.

OCCURRENCE OF WATER.

None of the outcropping formations considered in this paper have interstitial openings of sufficient size to permit the free movement of water. Examinations of seepage in quarries, mines, and natural outcrops show conclusively that the transmission of water in these formations is predominantly along solutionally enlarged joint planes. A minor amount of water is transmitted through solutionally developed bedding planes and joint openings which apparently have not been solutionally enlarged. Although of minor importance in the transmission of water prior to solutional development, the jointing is of paramount importance in providing the necessary initial openings along which solutional development can take place. K. K. Landes [1] has pointed out the apparent relationship of such solutional zones to dolomitization. Certainly the development of secondary porosity and permeability in such beds is largely a product of solutional processes. It is possible that oil accumulation in calcareous rocks found beneath uncomformities might be influenced by the presence of such zones of solution.

Strata of the Highbridge group yield water to wells only in the area where they are exposed to direct infiltration. As these rocks are exposed only along the Kentucky River, production of water from them is limited to that area. In all the areas where these strata are not exposed at the surface, virtually no water is produced from them. This is probably due to the effect of the bentonite beds in the Tyrone limestone, which prevent the passage of water down through the limestones of the Highbridge group.

The Lexington group carries more water than any other portion of the stratigraphic section. The Hermitage formation, the Benson limestone, and, to a lesser extent, the Jessamine formation are quite siliceous and shaly in some localities, and in those localities they do not yield water.

The Brannon limestone, because of its low solubility, exists throughout the area as a temporary base level for the process of solution, preventing the downward percolation of water and forcing it to move laterally to emerge in springs. For this reason, where the Brannon is present the underlying formations contain insufficient solutional openings to produce satisfactory yields of water.

The Woodburn and Perryville limestones, where exposed, yield water in large quantities; however, the shales of the overlying Cynthiana formation, present in most parts of these counties, generally prevent the accumulation of water in the Woodburn and Perryville limestones.

The Cynthiana formation includes the Nicholas limestone member which, like the Woodburn limestone, yields water only where the overlying shale has been removed.

The Eden shale has no solutional openings except where it is calcareous, and thus it rarely yields water.

[1] Landes, K. K.; Porosity through dolomitization: Am. Assoc. Petroleum Geologists Bull., vol. 30, no. 3, Mar. 1946.

Wells that yield water from these formations intersect one or more of these solutional openings at some point beneath the water table. Unless such an opening is encountered by drilling, the well will yield little or no water.

SOLUTIONAL FEATURES.

During the present investigation several hundred water wells have been studied. Comparisons of these well records seem to indicate a lack of solutional openings at depths exceeding 80 to 100 feet. In the 5-minute quadrangle just south of Lexington, between 37°55′ and 38°00′ north latitude and 84°25′ and 84°30′ west longitude, 27 water wells have been drilled. Of these, 20 have produced water and seven have been dry. Of the 20 wells producing water, none exceeds 80 feet in depth. Of the seven wells which do not produce water, one is 125 feet deep and the remaining six are 150

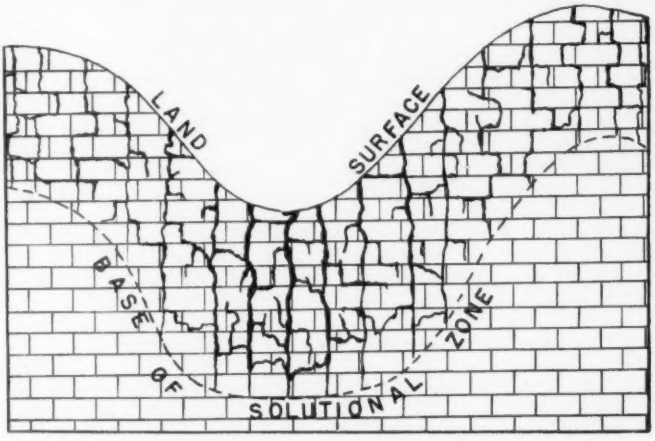

FIG. 4. The zone of solution in a valley.

feet or more in depth. Because all the dry wells exceed 80 feet in depth, it may be stated that 20 of 27 wells in this quadrangle reached water at depths of 80 feet or less. It may be further stated that no water has been produced in this quadrangle from strata lying more than 80 feet beneath the land surface.

As these wells have been drilled at locations representing a complete range of topographic conditions in an area of essentially flat-lying beds, it may be assumed that the zone of water production coincides more closely with topography than with the local stratigraphy or geologic structure. Such a statistical study would seem to indicate that there is little water below the depth of 80 feet because there are no solutional openings for such water. This suggests a zone of solution to a depth of about 80 feet or less, having its lower limit in a plane following approximately the configuration of the land surface.

Information obtained through the examination of several limestone mines indicates that solutional cavities were not present below a depth of about 90 feet. At the Central Rock Company in Lexington, Kentucky, a shaft has been sunk to a depth of 265 feet. At that depth mining has been carried out by means of the room and pillar method, over an area of about 800 by 800 feet in the Oregon limestone. In sinking the shaft, solutional openings in the limestone were encountered to a depth of 90 feet. Below this depth there were no further openings. Other limestone mines show similar conditions.

Figure 4 shows a hypothetical cross-section indicating the solutional zone near a valley as interpreted from present data, and Fig. 5 shows a similar section in a broad, flat upland area.

Abundant evidence for such solutional features as those shown in Fig. 5 below the upland limestone areas of the Lexington area is to be found through

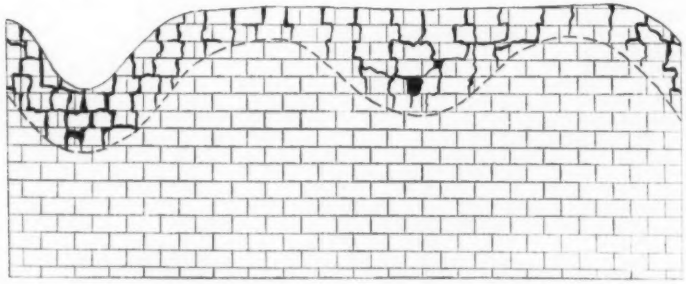

FIG. 5. The zone of solution in an upland area.

observation of the large underground streams which are exposed in the bottoms of deep sinkholes in these plateau areas. These underground subsequent drainage systems are the only form of drainage over much of the upland area.

In seeking an explanation of the development of the solutional zone, data were collected on the surface appearances of joint development. It became apparent that a process of directional development exists. In areas where the two sets of joints trend parallel and perpendicular, respectively, to a valley, the perpendicular set was greatly developed by solution (Fig. 6). This is due to the movement of water from topographic high toward topographic low. In the stream valleys both sets show equal development. This would show the tendency of ground water to move toward a valley and thence down the valley to some lower point of discharge. Assuming all other factors to be equal, the extent and depth of solution would depend upon the quantity of water involved. It would then be apparent, owing to the amounts and direction of movement of water involved, that the depth and extent of solution would be greater beneath the topographic lows.

Where two sets of joints intersect a valley in a diagonal pattern, the joints will be solutionally developed in a herringbone pattern pointing downstream (Fig. 7). An example of this type of solutional development may be seen in Ray's Fork, Scott County, 1 mile southwest of the intersection of Ray's Fork Road and U. S. Highway 25. The joints of the herringbone pattern pointing downstream are developed to a width of several inches.

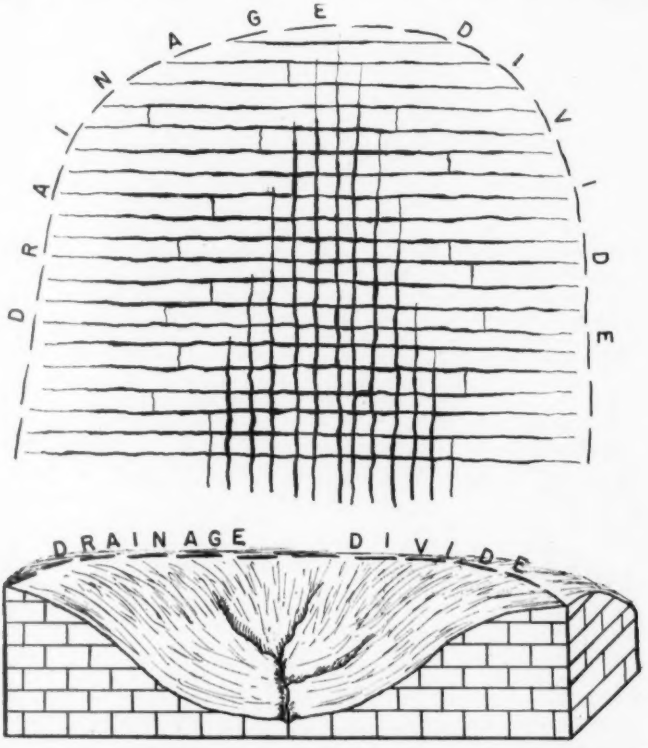

FIG. 6. Directional solution along joint planes accordant with drainage.

The herringbone pattern pointing upstream shows practically no solutional development, and the joints rarely exceed a quarter of an inch in width.

Two factors predominate in causing the shales and bentonites to serve effectively as local base levels for the processes of solution: (1) The lack of jointing in these somewhat plastic beds; (2) the lack of solutional enlargement of any openings in these beds. Where these beds of low permeability and solubility intersect the land surface, contact springs are produced and all water which penetrates to the depth of these strata is discharged at the surface

by springs and seeps. By thus preventing further downward percolation of these waters, the formation of solutional openings below these beds is prevented. Where these strata lie beneath the land surface, solution in a downward direction is prevented below their upper surface, and some lateral development is effected. Differences in the topographic, stratigraphic, and structural occurrence of these strata produce an infinite variety of solutional patterns.

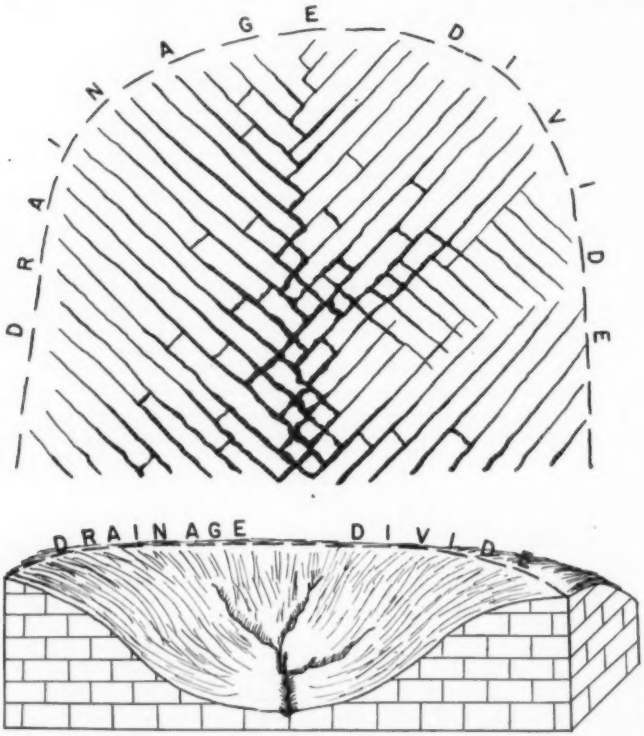

FIG. 7. Directional solution along joint planes discordant with drainage.

The intersection of an insoluble horizon with the bottom of a stream valley and its effect on solution are illustrated in Fig. 8. An example of this pattern occurs in Bourbon County, 1½ miles west of Paris, on U. S. Highway 40. In this locality the hilltops are underlain by coarsely crystalline limestone of the Benson limestone. The upper few feet of the Jessamine limestone, which is found at and below creek level, is a dense, fine-grained siliceous and shaly limestone which resists solution. Two wells have been drilled on hilltops into the Benson limestone. Both of these wells produce

water. One well has been drilled into the Jessamine limestone in the valley bottom, and it failed to produce water from either the upper or the lower portion of the limestone.

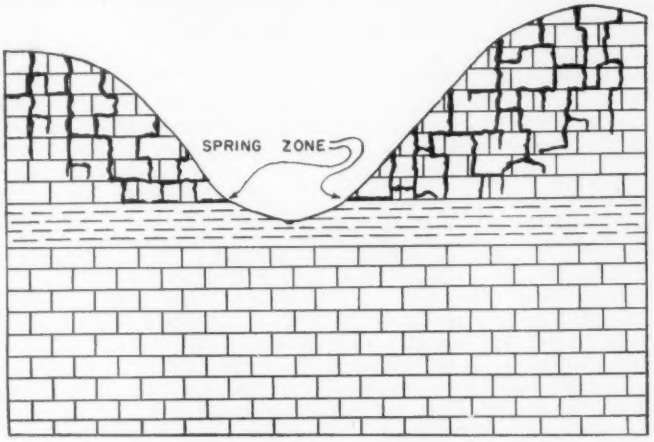

FIG. 8. Effect of insoluble stratum at stream level.

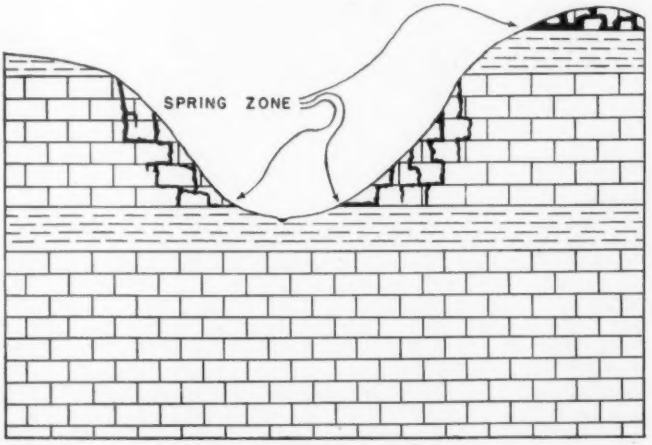

FIG. 9. Effect of insoluble strata at stream level and capping hill.

Figure 9 illustrates the presence of two insoluble horizons, one of which is at creek level and is relatively unbreached by the stream. An example of this pattern occurs near Shannondale in Fayette County. A well on the

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Mannelly farm was started on the hilltop, where it penetrated coarsely crystalline limestone of the Woodburn limestone, then the insoluble argillaceous limestone making up the Brannon limestone. After passing through the Brannon limestone the well passed through the coarsely crystalline Benson limestone, then through the insoluble upper portion of the Jessamine limestone, and finally ended in the coarsely crystalline lower portion of the Jessamine limestone. No water was produced from the well. Wells were drilled on the Kirkland and Powers farms at points topographically and stratigraphically lower. These wells begin just below the base of the Brannon limestone, and do not enter the Jessamine limestone. Both wells produce water from the Benson limestone.

Figure 10 illustrates the beginning of sub-stream solution as an insoluble horizon is breached by the stream valley.

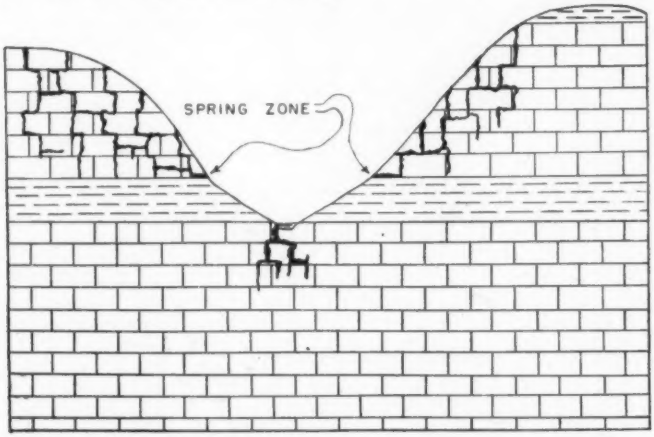

FIG. 10. Effect of insoluble stratum being breached by stream.

Figure 11 illustrates a condition encountered about 3¼ miles north of Lexington, on the Newton road. A well on the Moore farm starts in the Brannon limestone on the side of a hill and penetrates the Benson and Jessamine limestone without producing water. At the nearby Marks farm a successful well was drilled in the valley bottom, where the well starts and ends in the Benson limestone.

Figure 12 illustrates a similar condition but indicates an additional insoluble horizon at the top of a hill. An example of this feature occurs in Bourbon County in the vicinity of Hutchinson Station. A well drilled on the farm of I. S. Willmont, three quarters of a mile south of Hutchinson Station, started on the hilltop in the insoluble argillaceous limestone in the lower part of the Cynthiana formation, passed through this horizon into the coarsely crystalline Woodburn limestone and thence through the insoluble argillaceous Brannon limestone, and finally entered the crystalline Benson

limestone below. The well failed to produce water. A well on the nearby farm of I. Varellis was drilled in the creek bottom, in which the Benson limestone is exposed, and obtained water from that limestone.

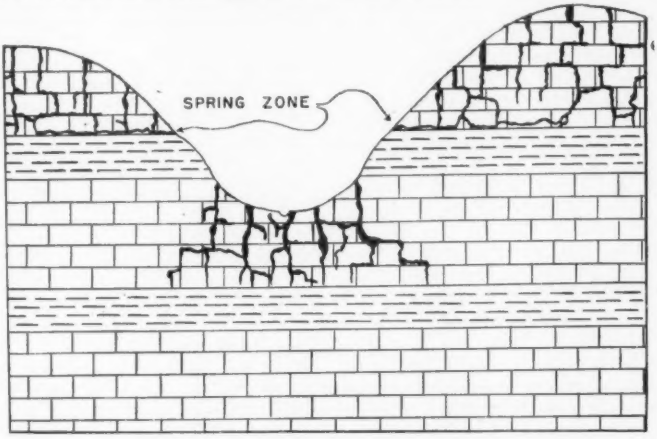

FIG. 11. Effect of insoluble stratum breached by stream.

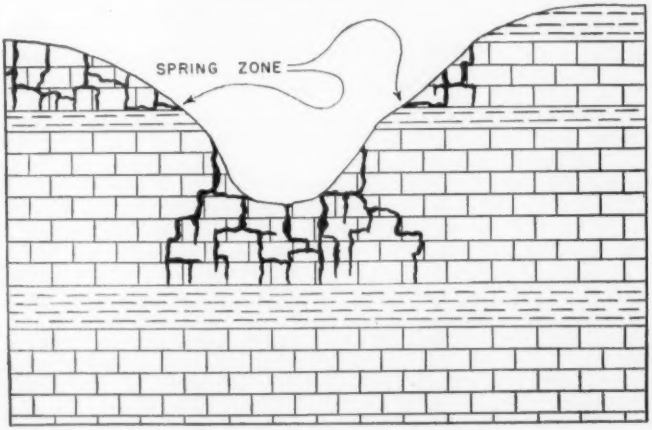

FIG. 12. Effect of insoluble strata below stream, breached, and capping hill.

It should be emphasized that these illustrations are merely a few specific examples of the many intricate combinations of topography and stratigraphy which combine to produce the areal solutional pattern. The records of the few wells used as illustrations are but a few of the hundreds of well records which further corroborate the conclusions indicated in Fig. 8 through 12.

CONCLUSIONS.

1. Water in this area is produced from solutionally developed joints and bedding planes and not from interstitial openings.

2. The greatest amount of solution has taken place beneath topographic lows.

3. Directional solution is an important feature of the development of underground subsequent stream patterns.

4. The most soluble beds and the most jointed of these soluble beds are likely to show the greatest solutional development and are, therefore, usually the most productive aquifers.

5. The accumulation of oil in limestones lying beneath unconformities may be closely related to such solutional features.

U. S. GEOLOGICAL SURVEY,
DEP'T OF GEOLOGY,
UNIVERSITY OF KENTUCKY,
October, 1947.

MINERAL RELATIONSHIPS IN THE ORES OF PACHUCA AND REAL DEL MONTE, HIDALGO, MEXICO.

EDSON S. BASTIN.

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ABSTRACT.

Representative collections of the richer silver ores from the famous Mexican districts of Pachuca and Real del Monte are now available mainly from Museum sources. Microscopic study of excellent collections from the U. S. National Museum reveals an unusual degree of uniformity in the character of the mineralization throughout the area. The primary mineralization represented a single episode characterized by a comparatively simple mineralogy. Pyrite, quartz, and sphalerite were the early hypogene minerals followed by hypogene galena, chalcopyrite, argentite and rarely polybasite and stephanite. The principal primary (hypogene) source of silver is unquestionably argentite. Native silver appears always to be secondary (supergene). Some argentite is also supergene.

THE Pachuca district in the State of Hidalgo, Mexico, is of especial interest to economic geologists as one of the world's greatest silver-producing areas which has been actively developed almost continuously from the time of the first discoveries in 1522 to the present day. The more general features of the region are fairly well known, having been described by the Mexican geologists Aguilera [1] and Ordoñez [2] and by H. V. Winchell,[3] Fred J. Pope [4] and Edward Wisser [5-6] among United States geologists. The last named writer deals primarily with the structural relations of the ore bodies.

[1] J. Aguilera y E. Ordoñez, El Mineral de Pachuca, Bols. 7, 8, 9, Instituto Geológico de Mexico, pp. 184, 1897.

[2] Ezequiel Ordoñez, The mining district of Pachuca, Mexico. Amer. Inst. Min. Met. Eng. Trans., XXXII: pp. 224–241, 1902.

[3] H. V. Winchell, Geology of Pachuca and El Oro, Mexico. Amer. Inst. Min. Met. Eng. Trans., LXVI: pp. 27–41, 1921.

[4] Fred J. Pope, Magmatic differentiation as a factor in the occurrence of ore shoots. ECON. GEOL., VI: pp. 503–511, 1911.

[5] Edward Wisser, The Pachuca silver district, Mexico. In Ore Deposits as Related to Structural Features. Edited by W. H. Newhouse. Princeton University Press, pp. 231–232, 1942.

[6] Edward Wisser, Formation of the North-South fractures of the Real del Monte area, Pachuca Silver District, Mexico. Amer. Inst. Min. Met. Eng. Trans., CXXVI, pp. 442–487, 1937.

Little has been written concerning the paragenesis of the ore minerals, and when the writer learned that a considerable collection of ores from Pachuca and the nearby camp of Real del Monte was available in the United States National Museum it seemed important to study these ores with the aid of the binocular microscope and the metallurgical microscope in the hope that significant additions to our knowledge of the conditions of origin of these famous ores might be obtained. The pages that follow report these results. The fact that most of the specimens were collected many years ago when richer ores from shallower depths were being mined than at present made the study more alluring.

The writer is indebted to the officials of the U. S. National Museum for the loan of the collections and in particular to Dr. Wm. F. Foshag of that Museum who might appropriately have made such studies, but generously encouraged the present writer to undertake them. The writer is also indebted to the Department of Geology at Cornell University for generously providing the necessary laboratory facilities.

GENERAL GEOLOGIC SETTING.

The mining camps of Pachuca and Real del Monte lie about 6 kilometers apart and 100 kilometers north of Mexico City. The Pachuca Range, 50 kilometers or so in length, of general N.W.–S.E. trend, and forming part of the Continental Divide, traverses the area. Pachuca, the larger of the two camps and the Capital of the State of Hidalgo, lies on the west side of the mountains at elevations of around 2400 to 3050 meters. Real del Monte lies on the eastern side of the range. Climatically the two camps contrast markedly. Pachuca is characterized by an average annual rainfall of around 11 inches, conditions are semiarid and vegetation is sparse. The east side of the range on which Real del Monte is located is characterized by an average annual rainfall of around 21 inches and by dense forests.

Geologically the two mining camps lie within a single geologic province characterized by Tertiary volcanic rocks. The region has been the locus of pronounced igneous activity, diastrophism, and mineralization, the three proccesses being closely linked in time. The surface rock over most of the area is an older augite andesite occurring mostly as thick flows and subordinately as tuffs and breccias—all with moderate dips. The older andesites are overlain locally by rhyolitic volcanics and these in turn by dacite flows. All of these volcanics are believed to be of middle Tertiary age and to have preceded the mineralization.

Within these volcanic rocks, particularly the relatively extensive older andesite, are east-west zones of extensive and profound hydrothermal alteration and it is within these altered zones that the mineral veins occur. Basalt flows overlie the more acid volcanics and are younger than the mineralization. Numerous dikes and stocks have been correlated with certain of the extrusives.

Two sets of fractures have been recognized, an older system best developed in the Pachuca area and characterized by strikes varying between N. 75 W. and E.–W., and a slightly younger system best displayed in the Real del Monte

area and characterized by North-South strikes. Both systems have steep dips. The largest ore shoots were found in the East-West veins and reached 1000 meters in length along the strike.

In Table I are listed the mines from which ores were available for study and the number of specimens from each.

TABLE I.

LIST OF MINES AND NUMBER OF SPECIMENS FROM EACH.

Pachuca District
- Amistad—2
- Barron—1
- Calderona—1
- Camelia—1 Maravillas Vein
- Dolores—5 Tapona Vein
- Guatimotzin—6
- Jacal—2
- La Rica—3 Viscaina Vein
- Porvenir—1
- Rosario—4
- Santa Ana—4
- Santa Margarita—1 Salvadora Vein
- Santa Rita—1
- San Jose de Gracia—2
- San Pedro—3
- Unknown—1
- A total of 15 or 16 mines and 38 specimens of which 21 were polished.

Real del Monte District
- Ahinchote—3
- Camelia—1 Maravillas Vein
- Carretaria—1
- Colon—1
- Difficultad—1
- Jesus Maria—1
- La Rica—1 Dios te Guie Vein
- Moran—4
- Sacramiento—2
- San Pedro y San Pablo—1
- Viscaina—6
- A total of 11 mines and 22 specimens of which 13 were polished.

PRIMARY OR HYPOGENE MINERALIZATION.

The ores of Pachuca and Real del Monte are characterized by relatively few hypogene minerals whose occurrence is repeated in specimen after specimen although their relative abundance may vary considerably. Rare and unusual minerals were not noted in the collection studied. Of the 34 polished specimens examined under the reflecting microscope only one showed evidence of fracturing during hypogene mineralization and other specimens from the same mine showed no such evidence. Cyclic repetitions of the mineral sequences do not occur. It must be concluded that hypogene mineralization constituted a single continuous episode. The volcanic rocks in which the ores were deposited were many of them fragmental rocks (pyroclastics) and the mineralization was guided by well defined zones of fracturing. Under such circumstances mineralization by the filling of open spaces must have been common but these spaces appear seldom to have been of large dimensions and the dominant mechanism of mineralization was replacement. One evidence of this is the very wide-spread dissemination of idiomorphic crystals of pyrite through the mineralized rocks. Most of this pyrite is not only idiomorphic toward all other ore minerals but its crystals are often of a larger order of size than the other minerals of the ore. In general the deposition of disseminated pyrite grains seems to have marked the initial stages in the mineralization process. This early pyrite was not destroyed or corroded in the later stages of hypogene mineralization although in places it yielded near the surface to supergene alterations.

There was no hiatus after the deposition of pyrite for some specimens show a clear overlap between pyrite deposition and that of sphalerite which in most of the ores is the dominant metallic mineral. Although the hypogene mineralization seems to have been continuous and progressive, its earlier stages were characterized by the deposition almost exclusively of pyrite, sphalerite and quartz. As already stated, in most of the specimens pyrite is older than either quartz or sphalerite but in some there is overlap. In many ores sphalerite prevailingly conforms to the hexagonal outlines of quartz and in others quartz seldom exhibits hexagonal outlines but conforms to the rotund outlines of sphalerite (Fig. 1). Commonly both relations can be observed in different parts of the same ore, clearly indicating an overlap in the time of deposition of the two minerals.

Following immediately after the deposition of pyrite, sphalerite and quartz came the deposition of the second and more valuable group of hypogene minerals, galena, chalcopyrite, argentite, with some polybasite and stephanite, and in some cases the gangue minerals calcite, rhodonite and fluorite. In most of the ores studied this group is prevailingly later than the pyrite, sphalerite and quartz to whose outlines they conform as is conspicuously shown in Fig. 2. In some specimens there is enough evidence of overlap between the members of the first and second groups to show clearly that there was no hiatus between their deposition. Only in a single polished specimen from the Guatimotzin mine at Pachuca was there evidence of slight fracturing between the deposition of groups 1 and 2. Among the minerals of group two there is only a little evidence of slight age diversity. Galena, chalcopyrite and hypogene argentite in particular nearly always occur in identical textural relations with respect to other minerals and show other evidences of contemporaneity.

As argentite is the principal valuable mineral of the ores its occurrence as a member of this second group requires special comment. Argentite was present in nearly all of the polished specimens and was recognized in a number of hand specimens through the binocular microscope. It is, therefore, a common mineral of these ores though much less abundant than the base-metal sulphides, sphalerite and galena. As described on a later page, argentite is found occasionally in these ores as a supergene replacement of other sulphides but its commonest modes of occurrence are as a component of the compact ores and as crystals in small vugs. In the vugs it may form fair-sized crystals between quartz crystals or small arborescent masses of very delicate crystals often in rosette-like aggregates.*

In the compact ores, argentite mostly occurs in textural relations that are identical with those of galena and chalcopyrite as shown in Fig. 2. It is also commonly found in delicate irregular intergrowths with chalcopyrite (Fig. 3). Contacts of argentite with galena and with chalcopyrite are mostly smoothly

* These delicate arborescent crystals are black, soft, sectile and malleable. When heated over a flame on a glass slide or when a blowpipe flame is applied to them they alter at once to arborescent forms of lustrous silver. When dissolved in nitric acid the addition of ammonium bichromate causes characteristic red and orange crystals of silver bichromate to form. The arborescent black crystals are therefore argentite. Such arborescent argentite was observed in ores from the Dolores, La Rica, Porvenir, Santa Ana and Santa Rita mines at Pachuca and from the Moran and Viscaina mines at Real del Monte.

curving. As the galena and chalcopyrite are unquestionably hypogene so is the associated argentite. Such argentite was found in nearly every polished specimen studied and there can be little doubt that for the district as a whole it is the principal source of silver. In a specimen from the Amistad mine at Pachuca much of the argentite occurs as small irregular areas in sphalerite. This argentite, however, is younger than the sphalerite for it is invariably bounded by crystal faces of the latter. In a few places, conformity of argentite to the crystal faces of chalcopyrite indicates that some of the argentite was younger than some chalcopyrite. In some of the compact ores, therefore, deposition of argentite may have continued longer than any other hypogene sulphide.

Coarse argentite is common as crystals in vugs, often filling in between quartz crystals, and also as patch-like coatings on the walls of late fractures. Some of the patch-like occurrences have a peripheral fringe of delicate arborescent argentite crystals. The argentite was generally the last mineral to be deposited in the vugs.

Certain less important relations of argentite will be described later.

The silver ores of Pachuca and Real del Monte are prevailingly fine- to medium-grained and highly quartzose. Massive or granular textures are common. In some ores pre-mineral brecciation of the wall-rock is well shown. In others banding with curving and often scalloped forms are well developed. It closely resembles that observed at Tonopah, Nevada, and like the Tonopah banding is believed to have developed during diffusion of the mineralizing solutions into the country rocks. A sawed ore surface 8 by 6 inches from the Guatimotzin mine at Pachuca is typical; in it the bands are ¼ to ½ inches wide, some of the bands being of fairly coarse white quartz, others an intergrowth of quartz and rhodonite, and others black and composed mainly of fine-grained sulphides. The scalloped form probably evidences a diffusion origin.

Crustification due to successive deposition on the walls of open spaces was well developed in ore from the Moran mine at Real del Monte, bands of white quartz free from sulphides alternating with dark bands rich in sulphides. The rarity of crustification supports the replacement origin of most of the ores.

While most of the ores studied are dense and compact a few are highly porous and some of these are very rich. Most of the porous ores with abundant small vugs seem to owe their porosity to partial or complete dissolving of calcite or dolomite gangue in or shortly below the oxidized zone. A specimen from 20 meters below the 290 meter level of the Santa Ana mine, Pachuca, is representative. Part of the specimen is compact and composed of sulphides in a quartz and carbonate gangue; other parts of the specimen are porous and largely leached of carbonates although quartz is unaffected. In the porous portion galena has been largely replaced by argentite. In some such porous ores, silver as wires and teeth is abundant as a supergene mineral.

The minerals that have been noted in the ores of Pachuca and Real del Monte are listed in Table II. Those starred were recorded by others but were not observed in the collections studied by Bastin. Significant features

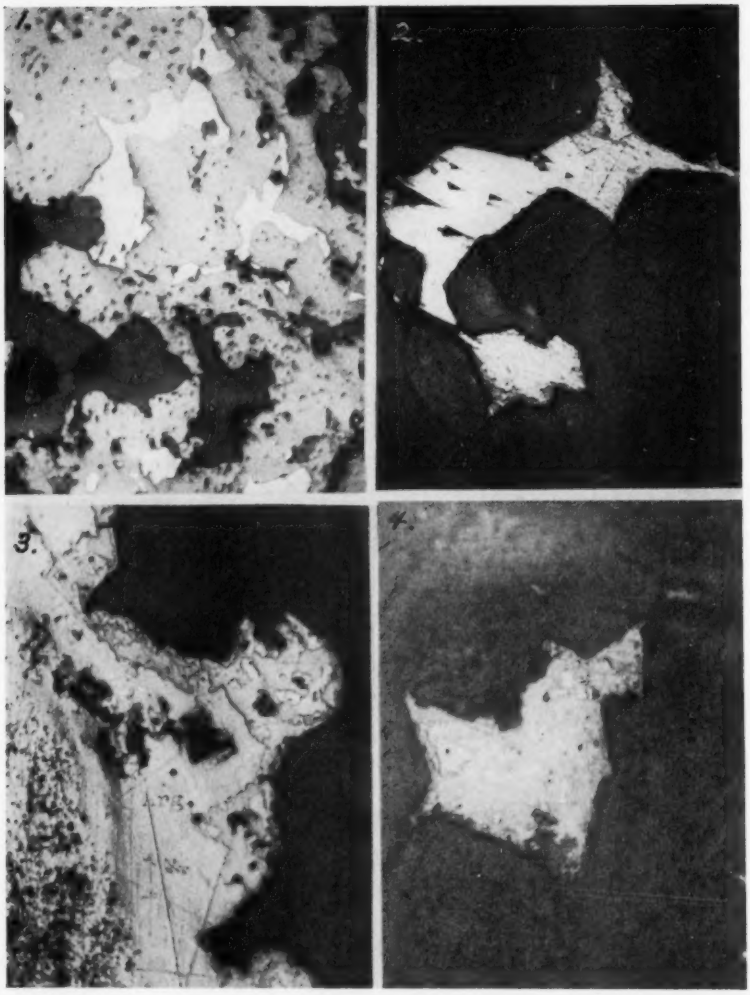

FIG. 1. Ore from the Guatimoczin mine, Pachuca. × 80. Both galena (white) and quartz (black) conform to the usually rotund outlines of sphalerite (gray).

FIG. 2. Ore from the Viscaina mine, Real del Monte. × 65. Galena (white with triangular pits) and argentite (mottled gray) both conform to the crystalline boundaries of older quartz (black). Galena and argentite are believed to be contemporaneous.

of the nature and occurrence of some of the minerals will next be briefly described.

TABLE II.

MINERALS OBSERVED IN THE ORES OF PACHUCA AND REAL DEL MONTE, HIDALGO, MEXICO.

S = Supergene only. R = Rare. * Reported by others.

- Elements
  - Silver—S
  - Gold*
- Sulphides
  - Argentite
  - Chalcocite—S
  - Bornite—S
  - Galena
  - Sphalerite
  - Chalcopyrite
  - Covellite—S
  - Pyrite
- Sulphosalts
  - Polybasite (arsenical)
  - Stephanite
  - Tetrahedrite—R
- Simple oxides
  - Quartz
  - Chalcedony
- Manganese oxides—S
- Multiple oxides
  - Limonite—S
- Haloids
  - Silver chlorides and bromides—S
  - Fluorite—R
- Carbonates
  - Calcite
  - Dolomite
  - Rhodochrosite *
  - Malachite—S
  - Azurite—S
- Silicates
  - Rhodonite
  - Adularia *
  - Sericite
  - Chlorite (Dolores mine, Pachuca)
  - Talc
  - Xonotlite *
- Sulphates
  - Barite
  - Anglesite—S

ORE AND GANGUE MINERALS.

Native silver appears to be almost invariably a supergene alteration of other silver minerals, most commonly of argentite. It commonly forms wires or teeth growing out of the older silver compounds. In ore from the Guatimotzin mine, Pachuca, native silver has in places replaced primary dolomite, the contacts being very irregular. *Gold* has been noted as a minor component of the limonitic oxidized ores.

Argentite occurs dominantly as a hypogene and subordinately as a supergene mineral. The details of its occurrence are sufficiently described elsewhere in this paper. It is the principal silver-bearing mineral of the ores.

Sphalerite in the ores of both districts is prevailingly of the light-colored or ordinary variety. In small part chalcopyrite occurs as small inclusions in sphalerite.

Sulpho-salts of silver include polybasite and stephanite. They occur mostly in vugs where they are associated with but less abundant than argentite. Stephanite was observed in ore from the Barron mine at Pachuca and

FIG. 3. Ore from the Viscaina mine, Real del Monte. × 100. The black areas are mostly quartz but in part small cavities. The abundant light gray mineral showing scratches is argentite (Arg.). The slightly darker gray mineral with which it is intergrown is chalcopyrite. This is interpreted as a primary contemporaneous intergrowth.

FIG. 4. Ore from Pachuca (mine not recorded) showing argentite and covellite occupying interspaces between older quartz crystals. × 65. The argentite (light gray) has been automorphically replaced by covellite (medium gray).

arsenian polybasite * in ores from the Barron, Camelia and Guatimotzin mines at Pachuca. The brittle silver minerals do not seem to be replacements of older minerals. Commonly they are implanted on quartz in vugs and in places wires and curling teeth of silver grow out of them. It seems probable that most if not all of the polybasite and stephanite is late hypogene. Ruby silver has not been noted in any of the ores.

Tetrahedrite was observed in a single specimen from the southern part of the Pachuca district. It was the only remaining primary metallic mineral other than pyrite in partly oxidized ore from the Amistad mine. Chemical tests showed antimony and copper but no arsenic and no silver.

Quartz, mostly white or colorless, is the dominant gangue mineral. Minor amounts of amethystine quartz occur in vugs. Chalcedonic silica is rare but was noted in ore from the Santa Rita mine at Pachuca and the Jesus Maria mine at Real del Monte. The latter was reddish brown with conchoidal fracture. *Manganese oxides,* found only in the shallow ores, have presumably resulted from the oxidation of rhodonite. They were noted in porous, limonitic ores from the San Jose de Gracia mine, Pachuca, from which all sulphides had been leached. Longitudinally striated prisms that appeared to be manganite were noted from the Carretaria mine at Real del Monte.

Calcite and dolomite are minor gangue minerals. They appear to belong among the later hypogene minerals. In the Rosario mine, Pachuca, calcite conforms to the crystal outlines of quartz and has partially and irregularly replaced galena beginning at grain boundaries of the latter.

Rhodonite is an abundant silicate in some of the ores. It was noted in ores from the Santa Margarita and the Guatimotzin mines, Pachuca. In the latter some pink bands are intimate intergrowths of white quartz and rhodonite. According to W. F. Foshag (personal communication) *adularia* occurs in microscopic crystals in some of the altered vein material.

Sulphates are rare in the collection studied. Barite was observed in vugs with quartz, as tabular white crystals in ore from the Viscaina mine at Real del Monte. Blue tabular crystals of barite, square in outline, occurred in vugs in ore from the Moran mine, Real del Monte.

Hypogene Mineral Relations.—In this list there is an absence of any hypogene minerals indicative of high-temperature conditions. Well crystallized quartz in vugs shows the hexagonal-tetartohedral habit indicative of crystallization below 573° C. The ores are probably correctly classed by Lindgren as epithermal.

Delicate microscopic intergrowths of some of the hypogene sulphides are fairly common. In ores from the Guatimotzin and Rosario mines at Pachuca chalcopyrite and argentite are intergrown in a pattern somewhat resembling graphic intergrowths though less regular. Similar intergrowths were observed in ore from the Camelia mine at Real del Monte. In ore from the San Pedro y San Pablo mine, Real del Monte, chalcopyrite is similarly intergrown with galena as well as argentite. Since in other parts of these same specimens chalcopyrite, galena, and argentite lie side by side in identical tex-

* The polybasite forms characteristic tabular, pseudo-hexagonal prisms with triangular striations on 001. It is black and brittle and reacts chemically for antimony, arsenic and silver.

tural relations these intergrowths are interpreted as the result of contemporaneous deposition (Fig. 3).

Replacements of early hypogene minerals by late hypogene are very rare but were conspicuous in one specimen from the Rosario mine at Pachuca. In this specimen calcite, of a notably smaller order of grain size than the older minerals, has replaced galena and chalcopyrite considerably and replaced sphalerite and quartz slightly. The replacement begins along contacts of grains of the same or different species but also penetrates along crystallographic directions notably of the chalcopyrite and the galena (Fig. 5). In certain areas the replacement has been almost complete and areas that were originally quartz, chalcopyrite and galena are now calcite "dusted" with tiny replacement remnants of these three minerals. Pyrite seems to have resisted the replacement. The replacement of quartz indicates that the replacing solutions were alkaline and they are believed to have acted in the late stages of hypogne mineralization.

Supergene Enrichment.—Supergene enrichment was recognized in many of the specimens studied. The depths from which these came was seldom recorded. Some show evidences of oxidation but most do not and evidently came from below the ground water table. Enrichment in copper in places involved automorphic replacement of chalcopyrite by covellite in bladed crystals beginning at the peripheries of the chalcopyrite grains; elsewhere chalcocite is the replacing mineral or rarely bornite. Not uncommonly supergene copper minerals replace *non-cupriferous* hypogene minerals. In some ores covellite replaces galena or more rarely forms ragged replacement veinlets in sphalerite or replaces the sphalerite along quartz or galena contacts (Moran mine, Real del Monte). Not uncommonly galena has been replaced by a fine aggregate of covellite and anglesite probably in accordance with the equation $PbS + CuSO_4 \rightarrow PbSO_4 + CuS$. In ore from the Rosario mine, Pachuca, supergene covellite in bladed crystals automorphically replaces argentite (Fig. 4). Enrichment in silver was, in the shallow ores, an important factor in increasing the commercial value of the ores. Replacement of chalcopyrite by argentite was well shown in a specimen from the Barron mine, Pachuca. The replacement began at the original contacts of chalcopyrite with quartz or galena and penetrated the chalcopyrite until only small and generally rounded relics of chalcopyrite remained. Some covellite may be associated with this argentite and is apparently of the same age. Replacement of galena by argentite was conspicuous in a hand specimen from just below the 290-meter level of the Santa Ana mine, Pachuca. Parts of this specimen are fairly compact unaltered sulphides, mainly galena, chalcopyrite and sphalerite, with quartz and calcite and numerous but very small vugs. The remainder of the specimen has been leached of most of its calcite so that it is highly porous. In the compact portions of the specimen galena is recognizable in vugs by its brittleness, cubic form, and cleavage. It shows incipient replacement by argentite along cleavages. In those parts of the specimen that are more porous from the dissolving of calcite, galena seems at first sight to be lacking and in its stead are cubic crystals of black, sectile argentite. When these cubes are broken open, however, they are found to contain irregular, brittle, cleavable

cores of galena. It is evident that there has been a partial replacement of galena by argentite. Whether this replacement was contemporaneous with the leaching of the calcite or was later is uncertain.

In a single specimen from the San Pedro y San Pablo mine at Real del Monte there was a slight replacement of sphalerite by argentite, just sufficient to make an occasional contact ragged whereas most sphalerite contacts are smooth. It is uncertain whether this replacement is supergene or late hypogene.

The supergene replacements are initiated along contacts of mineral grains but not all such contacts are equally favorable. In a polished specimen from the Guatimotzin mine, Pachuca, replacement of chalcopyrite by covellite starts peripherally at quartz contacts and is much less common at sphalerite and galena contacts (Fig. 6). As chalcopyrite is the only mineral replaced, this preference is probably a matter of the tightness of the contacts. In places, these relations are quite striking. Similar preferences for quartz contacts were observed in several other ores. Interpreted in chemical terms, the replacements just described indicate that copper sulphate-bearing solutions formed by near-surface oxidation of the copper-bearing sulphides descended into the ground water zone and there reacted with the primary ore minerals to form secondary copper minerals in accordance with reactions of the following types:

$$CuFeS_2 + CuSO_4 \rightarrow 2\ CuS + FeSO_4$$
$$ZnS + CuSO_4 \rightarrow CuS + ZnSO_4$$
$$PbS + CuSO_4 \rightarrow CuS + PbSO_4$$
$$Ag_2S + CuSO_4 \rightarrow CuS + Ag_2SO_4.$$

Copper is redeposited as covellite, chalcocite, and rarely as bornite. Iron and zinc thus taken into solution as sulphates were probably not reprecipitated within the ore bodies. Silver carried downward as the fairly soluble sulphate was reprecipitated as supergene argentite through replacement of chalcopyrite as observed in ore from the Barron mine, Pachuca, or reprecipitated as argentite by the replacement of galena as noted in ore from the Santa Ana mine, Pachuca, in accordance with some such equation as $PbS + Ag_2SO_4 \rightarrow Ag_2S + PbSO_4$. Other mechanisms are also available for the precipitation of the silver.

Paragenesis.—Some precipitation of late argentite took place, not by replacement, but by deposition in vugs on quartz or along fractures in altered wall-rock. In a specimen from the Viscaina mine, Real del Monte, argentite masses up to 0.5 cm in diameter lie on or between crystals of white quartz as the youngest vug mineral. Some of this argentite shows automorphic crystal faces but some shows rounded surfaces as if corroded. In many of the ores lichen-like patches of argentite, up to ¼ mm or so in thickness, have been deposited indiscriminately on supergene sulphides or on gangue minerals along small fractures. These patch-like masses commonly pass at their borders into delicate arborescent fringes or clusters of argentite crystals. As argentite is among the youngest of the hypogene minerals it is almost certain

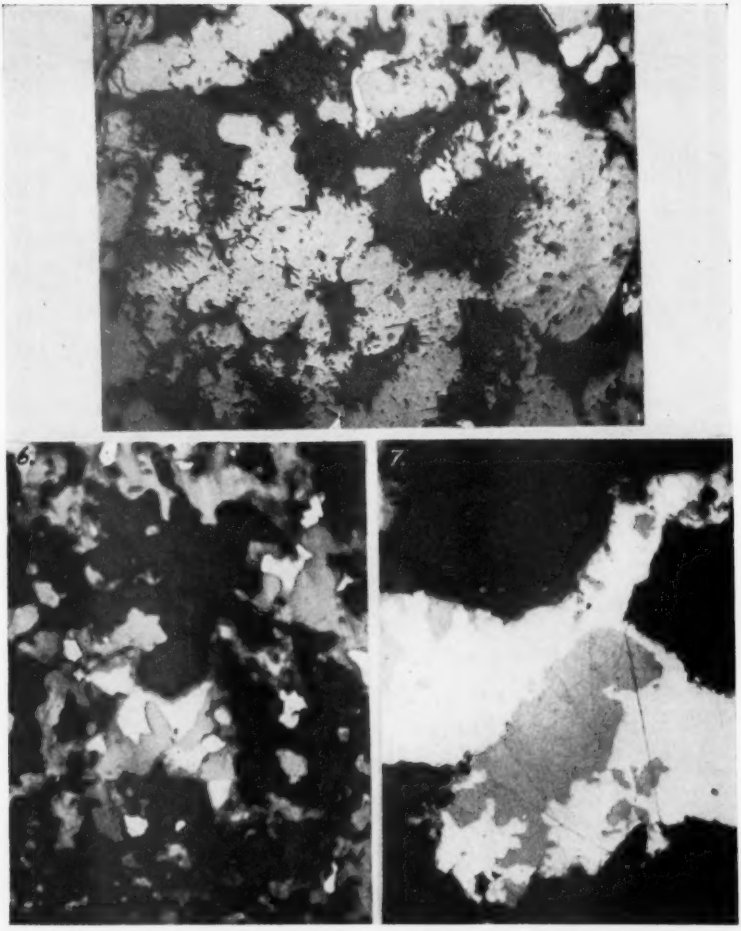

FIG. 5. Ore from the Rosario mine, Pachuca, in which calcite (black) has partially replaced galena (white) and chalcopyrite (gray) with the formation of very irregular boundaries. × 90.

FIG. 6. Ore from the Guatimotzin mine, Pachuca. × 80. Dark gray is quartz. White is chalcopyrite and smooth medium gray is sphalerite. Near the center of the figure rims of covellite (mottled gray) have developed by the replacement of chalcopyrite along quartz contacts while they are absent along the contacts of chalcopyrite with sphalerite.

FIG. 7. Ore from the Barron mine, Pachuca. × 80. Argentite (medium gray) has been replaced by native silver (white) with the development of very irregular contacts.

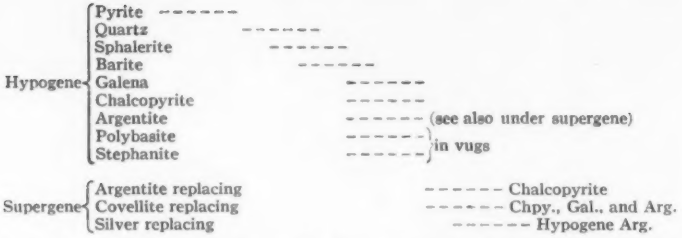

FIG. 8. Paragenetic sequence in specimen from the Barron mine, Pachuca.

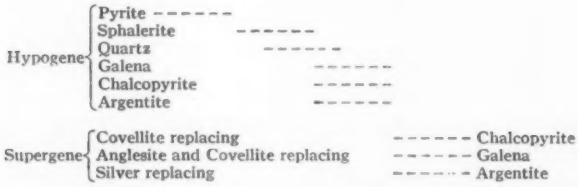

FIG. 9. Paragenetic sequence in ore from Guatimotzin mine, Pachuca.

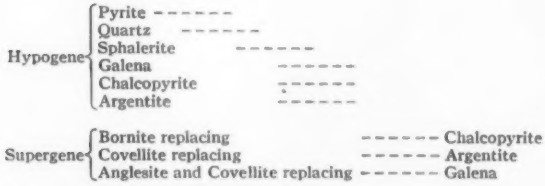

FIG. 10. Paragenetic sequence in specimen from Sacramiento mine, Real del Monte.

* A few chalcopyrite inclusions in sphalerite.

FIG. 11. Paragenetic sequence in specimen from San Pedro y San Pablo mine, Real del Monte.

that some would be deposited as a late hypogene mineral in vugs and fractures. Whether any of this argentite is supergene is uncertain. In the absence of any visible precipitating agent the chemistry of its deposition is more easily explained by deposition from cooling hypogene sulphide-bearing solutions than by deposition from cool supergene sulphate-bearing solutions.

One undoubted instance of deposition of supergene argentite was found in ore from the San Pedro mine, Pachuca. In porous, oxidized ore from this mine wires of silver have been converted into black argentite superficially but are still silver internally and the wire form is preserved. It is probable that hydrogen sulphide was the agent of this change.

The forms of argentite just described, occurring in vugs and fractures, are the principal sources of the native silver. By its alteration in contact with air in the zone of oxidation the sulphur is oxidized and wires and curling teeth of silver grow out of the argentite. No native silver that could be interpreted as hypogene was found in the ores.

Except for the formation of native silver (Fig. 7), oxidation phenomena were not well displayed in the collection studied, most of the specimens obviously coming from deeper than the oxidized zone. A little malachite was occasionally observed in vugs and chalcanthite along fractures, as were limonite and oxides of manganese.

Paragenetic sequences in mineral deposition in two representative ores from Pachuca and two from Real del Monte are shown in Figs. 8 to 11. It should be noted that all the lines in these diagrams are of the same length. The diagrams indicate which minerals were deposited early and which were deposited later but imply nothing of the time interval over which any one mineral was deposited. Pyrite deposition, for example, may have been a long episode and the period of argentite deposition relatively brief.

ITHACA, N. Y.,
December 1, 1947.

DISCUSSION AND COMMUNICATIONS

DOMESTIC SOURCES OF PIEZOELECTRIC CRYSTALLINE QUARTZ.

Sir: An adequate supply of crystalline quartz of piezoelectric grade and size continues to be of fundamental importance to the U. S. Army Signal Corps. Current electronic development programs of the Armed Forces depend upon the use of quartz crystals in all applications where accurate frequency control is necessary. In peacetime this may not seem too significant, but in planning for possible national defense emergencies, an adequate supply of piezoelectric grade raw quartz is just as important as an adequate supply of some of the more publicized strategic minerals.

Prior to World War II, the Signal Corps accepted the use of quartz crystals for frequency control purposes in essentially all electronic communication, navigation and radar equipment operating in the audio and radio frequency spectra up to and including the ultra high frequency channels. Some equipments required a complement of 100 or more crystal units plus spares and replacements for satisfactory operation. As a result, over 70,000,000 crystal units were manufactured for the Army, Navy and Air Forces, requiring over 4,000,000 pounds of radio grade quartz, between January 1942 and V–J Day. Use of such a large quantity of crystal units was necessary in order to establish and maintain, with a minimum of effort, clear and definite frequency channels of greater stability than could be obtained by any other means. This policy was justified on the basis that quartz was without a peer as a frequency controlling element. Military and civilian uses of quartz in the field, as well as laboratory studies, have confirmed this premise and as of this date, no means of highly stable frequency control, superior to quartz, has been discovered. It appears certain that the demand for use of quartz for frequency control purposes will continue at a high level because its outstanding value in this service will be a strong consideration and determining factor in development and use of military electronic equipment.

One of the greatest difficulties in the past use of quartz has been that of supply. The only dependable source of acceptable raw material has been Brazil. During World War II, it was necessary to ship the quartz over difficult supply lines, including marine transportation subject to enemy naval attack. Late in 1942, this became such a serious problem that it was necessary to ship the quartz by air freight, which limited the quantity obtainable. That situation was alleviated somewhat by the clearing of the sea lanes through the Caribbean in 1943, but at no time since has this country been free of the necessity of stock-piling quartz for strategic purposes. "Quartz Crystal" has been listed invariably during the past two years as a "strategic mineral" on

every public tabulation of minerals that must be stock-piled. Some relief from quantity requirements in the future may be obtained through design of equipment requiring fewer crystal units, use of substitutes for natural quartz, design of more dependable crystal units that would require less replacement, conservation of quartz through improved manufacturing methods, greater utilization of lower grade quartz, and design of crystal units utilizing less quartz. A program for conservation of this nature was initiated by the War Department, Office of the Chief Signal Officer in 1943, and was subscribed to throughout the duration of hostilities by all the agencies responsible for the use of piezoelectric grade quartz. This program resulted in an increased yield of eighty percent per pound of quartz consumed. It is intended that this policy continue in effect insofar as Government uses are concerned.

Quartz is not the only piezoelectric crystalline material. Over one hundred and seventy-five substances have been reported by various investigators to have piezoelectric properties in varying degrees. Any crystal having no center of symmetry should be piezoelectric although many (such as cinnabar) are electrically conductive and therefore cannot be used for electronic frequency control purposes. Practically all the other substances have various physical properties that make them unsuitable for frequency control applications. Three other minerals which offer promise for electronic, piezoelectric use are crystalline tourmaline, nepheline and berlinite. However, none of these materials appear to occur plentifully in nature in suitable form. Tourmaline, for piezoelectric use, must be of the non-iron-bearing variety. Nepheline and berlinite apparently do not occur in large, well formed crystals. The Signal Corps Engineering Laboratories would be interested in any information concerning the location and quantities of any of these minerals occurring in large, crystalline form, relatively clear and free from defects.

The Signal Corps has been so concerned over the future natural quartz supply for piezoelectric frequency control application, that it has launched a program for synthesis of substitute materials. Brush Development Company of Cleveland, Ohio, and Antioch College, Yellow Springs, Ohio, are well along on quartz synthesis. Edward Washken of Cambridge, Mass., is engaged in research for synthesis of nepheline and Baird Associates of Cambridge, Mass., is engaged in research for synthesis of tourmaline. The University of Minnesota and Squier Signal Laboratory of Fort Monmouth, N. J., are investigating the synthesis of berlinite. These projects (with the exception of Squier Signal Laboratory) are being sponsored by means of contracts with the Signal Corps Engineering Laboratories. The Naval Research Laboratories are making major contributions to piezoelectric crystal synthesis. Results to date have been gratifying but in no way affect the present Signal Corps desire to promote consideration for radio grade quartz wherever explorations of any kind are conducted in Central and North America.

It is well known by geologists, mining engineers and mineralogists that quartz is one of the most abundant mineral constituents of the earth's crust; large quantities occur throughout Central and North America. Unfortunately, piezoelectric use of quartz is very exacting in its requirements, thus limiting usable quartz to only one of many varieties. It must be crystalline

and must be essentially eye clear, free of impurities, physical defects and crystallographic variations, including twinning, within any given crystal. The dimensions of operating crystal plates and the manufacturing methods have limited the physical size of the quartz crystals heretofore used to a minimum of 100 grams by weight having a length parallel to the vertical crystallographic axis of at least two inches and a diameter, perpendicular to the vertical crystallographic axis, of at least one inch. Quartz of this size must exhibit at least one identifiable crystallographic face for economical use, although crystals over 200 grams can be economically processed whether "faced" or not. Obviously, the piezoelectric grade of this important mineral is rare in occurrence in sizeable deposits. Limited, known sources in North and Central America have been confined largely to uneconomical deposits in Guatemala, Arkansas and California. Usable crystals have been found singly or in very small quantities scattered throughout Central and North America and it is a reasonable geologic assumption that satisfactory sources, as yet undiscovered, may exist in these regions. Continued geologic exploration may be expected to reveal such sources; especially is this true when it is considered that much investigation of this nature remains to be done in some of the more remote or inaccessible localities (*e.g.*, Alaska). Large deposits of piezoelectric grade quartz, even in Continental United States, may exist and this possibility cannot be dismissed.

Military and civilian officials of the Signal Corps have recognized and discussed the problems covered in the preceding paragraphs during the past several years. An active program on the part of the Signal Corps Engineering Laboratories calls for continuous liaison with the Geological Survey, Bureau of Mines, other Government Organizations, including State Surveys, Geological and Mineralogical Societies, Educational Institutions and Mining Organizations. These groups, as well as individuals, are asked to be on the alert for sizeable bodies of radio grade quartz and to advise the Commanding Officer, Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey, of such findings. Signal Corps representatives will examine any North or Central American piezoelectric mineral source localities in coordination with the other interested Government agencies or groups indicated if warranted. Quartz so located will be tested by the Signal Corps Engineering Laboratories for piezoelectric qualities. These Laboratories would also be interested in information regarding relatively large deposits of crystalline quartz of individual crystal sizes in the range of 30 to 100 grams.

HUGH H. WAESCHE.

GEOLOGIST, SIGNAL CORPS ENGINEERING LABORATORIES,
FORT MONMOUTH, N. J.
Dec. 20, 1947.

REVIEWS

Geologia e Genesi delle Bauxiti (Geology and Genesis of Bauxite). By ANTONIO CAVINATO. Pp. 50; figs. 12. Padoue, 1947.

This work is the fruit of the author's original studies on Italian and foreign bauxite, and is also the conclusive result of his personal considerations.

The first chapters are compilative and deal with the non-controversial features of the geology and genesis of bauxite. This leads the author to enunciate some general rules on the geologico-stratigraphic conditions of bauxite deposits, which are here formulated for the first time. The results of eight unpublished analyses are also reported.

Chapter I deals with the various processes of desilication and the natural breakdown of aluminum silicates. The author does not consider the latter as an ordinary geochemical phenomenon similar to the decomposition of the iron, manganese and magnesium silicates, or others. There are many genetic assumptions possible: laterization in place, alteration of a lateritic deposit—with or without transportation—, sulphatization in place and reduction of the sulphates in situ, transportation of sulphates in solution and reactions with limestones, transportation in colloidal solutions of the hydroxides and their coagulation in marine, lake or marshy basins, slow lixiviation of the argillaceous deposits, or of the marly limestones with removal in solution of the limestone and desilication of the clay, etc.

Chapter II is a descriptive account of some bauxite deposits and their different characters. Deposits derived from intrusives in Guiana, Madagascar, India, Seychelles; Arkansas bauxite associated with syenite and derivated by superficial alteration during the Tertiary; German bauxite on basalt; Malabar bauxite from gneiss; bauxite associated with Cretaceous-Eocene rocks in the Mediterranean basin; bauxitic and ochreous-ferriferous deposits "transported" or "detritic."

Chapter III shows there is no such thing as a metallogenetic era of bauxite, as there are Silurian and Carboniferous (Turkestan, Gold Coast, Urals), with Devonian clay (North Ural), Triassic (Dalmatia), Jurassic (Russia), Cretaceous-Eocenic (Mediterranean basin), Oligocenic (Russia) and some Quaternary.

Chapter IV contains descriptions of some bauxite deposits of the Mediterranean basin (Abruzzo, Dalmatia, Croatia, Puglia, Istria) and of other countries (Turkey, Hungary, France).

In the phase of emergence (epirogenic or orogenic, and between Neocomian and middle Eocene) the phenomena of spoliation, incarceration, levelling and the formation of the paleosoil were completed. In surface depressions the hydroxides and hydrosilicates of aluminum and iron were deposited, and eventually they occupied pockets, sinkholes or other surface depressions in clay; or else they may have occupied the interstices of conglomerates. The bauxite, being covered by conglomerates, clay, or sand before the marine invasion occurred, did not suffer from wave action; perhaps also it was already coagulated and hardened in the prolonged emergence period.

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Chapter V is an account of the chemical and mineralogical composition of the bauxite; also the diagenesis and metamorphism, texture and structure. The variability of the chemical and mineralogical composition of the bauxite deposits is noteworthy. There is no set boundary between clay and bauxite, but a gradual change from one to the other; there is also a gradual change from arenaceous to bauxitic materials, from ferriferous to bauxitic-ferriferous, and from manganiferous-clayey to bauxitic materials. The actual clayey, ferriferous, manganiferous, bauxitic, lateritic deposits disappear by the merging of one into the other, or merge along the strike into marl, sand, clayey sand or red earth.

The genesis of the bauxite deposits is discussed in Chapter VI. Those of the Mediterranean basin are considered under: a metasomatic origin (by reaction between sulphate and clay); insoluble residues; deterioration and transportation of the lateritic crust; eolian transportation; desilication in place; and a hydrothermal origin which the author does not reject. An endogen autochtone genesis of bauxite (Coquart, 1871) is unacceptable to the author.

The author's conclusions are: The bauxitic deposits have in general a lake facies "in the same way as argillaceous deposits." The hydroxides and hydrosilicates that compose the bauxite deposits come mainly from the destruction of laterite by superficial alteration of the aluminum and ferrous silicates. "In the same way as the argillaceous deposits" is justified, if not confirmed, by the often repeated fact that the bauxite deposits of each geological age are generally accompanied by clay; that the chemical and mineralogical composition of either bauxite or of the clays result from a mixture of the hydroxides and hydrosilicates in variable proportions; and that there exist all transitions from clay to bauxite. An alluvial, eluvial, fluvial, glacial, eolian or marine facies is excluded for primary bauxite deposits, because they have a lake facies.

Erosion and transportation of the primary bauxite deposits has given rise to secondary bauxite deposits, such as detrital and sedimentary deposits, and also many other variations, such as apparent layers filling cavities, crevices, or pockets in limestone or other rocks.

The bauxite deposits of each geological age are distributed along erosion surfaces. They were deposited during phases of the emergence of continents and rest directly on eroded surfaces, in places in depressions in limestone; or else they rest on other continental or lake sediments such as conglomerate or clays, or on other rocks.

A marine facies, which is an exception to this rule, is not excluded, but certain reservations must be made.

The genesis of bauxite has been much discussed, but, the author believes, with insufficient clarity. He believes it necessary to affirm that the unsolved problems are no longer the geological ones relative to the facies, to the era (although doubt remains concerning the so-called lateritic deposits), to the "geometric allure" of the accumulation, to the extent of the deposits, to the geochemical desilicating processes, but rather the problems relative to establishing the site of origin of the material, the agent and mode of the transportation (whether it is transported in solution or in suspension), the mode of redeposition, and the selection and alteration that may be accomplished during the transportation.

At the end the author describes succinctly the morphology of the bauxite deposits and the tectonics of bauxite, and there is an appendix on the origin of the red earth and of the iron deposits of Istria.

M. L. MIGNONE.

Textures of the Ore Minerals. By A. B. EDWARDS. Pp. 185; figs. 154. Australian Institute of Mining and Metallurgy, Melbourne, Australia, 1947.

This is the only modern book that deals with the textures, mineral relations and geologic thermometry of the ore minerals. It is not to be confused with books on opaque mineral identification such as Short's "Microscopic Determination of the Ore Minerals," Schneiderhohn and Ramdohr's "Lehrbuch der Erzmikroskopie" or even Van der Veen's "Mineralography and Ore Deposition." These books deal largely with microscopic determinations of the opaque minerals and ore mineral textures are incidental. This volume by Edwards, however, does not take up mineral identification but deals with textural relations and their origins.

The following chapter headings give some idea of its contents: Textures of Native Metals; Primary Zoning and Banding in Oxide and Sulphide Ores; Textures due to Deformation; Solid Solutions (in native metals, oxides, and sulphide and sulphosalt minerals); Replacement Textures; Application to Ore Geology; Application to Ore Dressing; The Transparent Gangue Minerals. An index to authors, localities and subjects is helpful.

The book is well illustrated with plates (on coated paper) depicting the various textures, most of which are drawn from Australian literature and occurrences. Particularly valuable parts of the book are the discussions of the crystallographic controls of textures and the conditions under which the various textures are formed, especially the temperature-pressure conditions. Thus, much valuable geologic thermometry of the ore minerals is compiled under one set of covers.

The book is one that every economic geologist will wish to own and he will find himself referring to it constantly. The author is to be congratulated.

A. M. B.

Principles of Micropaleontology. By MARTIN F. GLAESSNER. Pp. 296; figs. 64; pls. 14. John Wiley & Sons, New York 1947. Price, $6.00.

This volume was first published in Australia in 1945, followed by this American edition in 1947.

The author was educated in Vienna and joined the Geology Department of the Vienna Natural History Museum. Later, he was Senior Research Officer at the State Petroleum Institute and Mineral Fuels Institute of Moscow's Academy of Science, lecturing at the Paleontological Laboratory of the University of Moscow. In 1938 he joined the staff of the Anglo-Iranian Oil Co.

Part I, Chapters 1 to 3, the Origin and Present Status of Micropaleontology, and Microfossils. Part II deals with the paleontology of the foraminifera, their life history, classification, and paleo-ecology. Part III takes up stratigraphic micropaleontology under stratigraphic sequence, correlation of sedimentary rocks and oilfield practice. There is an appendix of Classification of Foraminifera and one of Bibliography.

The book should be of great interest to all paleontologists, both teachers and field workers. Likewise, it will interest all petroleum geologists because of the discussion of oilfield practice in Europe and Asia.

American Oil Operations Abroad. By LEONARD M. FANNING. Pp. 270; illust. McGraw-Hill Book Co., New York, 1947. Price, $5.00.

This book by the Editor of "Our Oil Resources" tells a story of the search for oil by Americans in foreign countries and gives the reader an idea of the international oil situation, which lately has been so much to the front.

The chapter headings are: America Looks Abroad for Oil; Number One Risk—Politics; Expropriation and Seizure; Time Lags that Mean Millions; Struggle for Share of World Oil; Caribbean Oil; Oil Spotlight on Middle East; American Position declines in Foreign Markets; Complex American Position in Foreign Markets; Advantages of Foreign Oil Operations to our Economy; Economic, Social and Educational Advantages to Foreign Nationals; Our Future Oil Participation; Appendix: American Foreign Petroleum Interests; U. S. Reserves; Anglo-American Oil Agreement; Foreign Oil Statistics.

The book with its many pictures, charts and tables interweaves much factual data with the romance of oil exploration. It is written in an engaging style and is a good companion to "Our Oil Resources."

BOOKS RECEIVED.

ALAN T. BRODERICK.

Mesozoic Fossils of the Peruvian Andes (Ellsworth Expedition Publication). M. M. KNECHTEL, E. F. RICHARDS, M. V. RATHBUN. Pp. 150; figs. 24; pls. 50. Johns Hopkins University Studies in Geology No. 15. Baltimore, 1947.

Minerals of Arizona. F. W. GALBRAITH. Pp. 101. Ariz. Bur. Mines, Geol. Series No. 17, Bull. 153. Tucson, 1947. *Mineral-by-mineral listing of Arizona localities.*

Post-Devonian Igneous Activity in Southeastern Missouri. A. L. KIDWELL. Pp. 83; figs. 2; pls. 7; table 1. Missouri Geol. Survey Rep. of Investigations No. 4. Rolla, 1947. *Small ultrabasic dikes and pipes, some of which are diatremes.*

Bibliography of the Geology and Mineral Resources of Oregon (Supplement) July 1, 1936, to December 31, 1945. J. E. ALLEN AND OTHERS. Pp. 110. Oregon Dept. Geol. and Mineral Industries, Bull. 33. Portland, 1947. *Over 1000 titles. Not annotated.*

Geological Survey of Wyoming. Laramie, 1947.

Bull. 38. Stratigraphic Sections of Mesozoic Rocks in Central Wyoming. J. D. LOVE AND OTHERS. Pp. 59; figs. 8. *Detailed descriptions of the lithologic units in 7 representative sections in the Wind River Basin.*

Bull. 39. Phosphate Deposits near Lander, Wyoming. R. H. KING. Pp. 84; figs. 6; pls. 3. *2 major zones in Permian Phosphoria formation. Reserves: Upper zone, 3′ to 6′ thick, 100,000,000 short tons of 35% bone phosphate of lime (low grade) above drainage; 13,825,000 tons for each 100′ below drainage. Lower zone, 3′ to 4′ thick, 30,000,000 tons of 52% B.P.L. (medium grade) above drainage, 3,780,000 tons for each 100′ below drainage.*

An Investigation into the Value of the Seismic Methods in Delineating Structure in Southwestern Ontario. J. H. HODGSON. Pp. 32; figs. 7; tbls. 4; photos 6. Ontario Dept. Mines 56th Ann. Report, Vol. 56, part 4, 1947. Toronto, 1947. *Failure of seismic methods due to low reflection coefficients, very high reflection velocities, complicated surface conditions, thin Paleozoic section.*

Australia Solid Geology. J. GENTILLI. University of Western Australia. Nedlands, W. A. *Uncolored areal geology map of Australia, scale 1″ = 100 miles.*

Index for Volume 34 (1931) to 43 (1940) of the Geological Society of South Africa. A. L. HALL, J. DE V. LITTLE. Pp. 266. Trans. and Proc. of the Geol. Soc. of S. Africa. Johannesburg, 1947.

The Mineral Resources of Tanganyika Territory. E. O. TEALE AND F. OATES. Pp. 172; tbls. 20; maps 2 (1 geology, colored, 1:4,000,000). Tanganyika Dept. of Lands and Mines, Geol. Div. Bull. 16. Dodoma, 1946. *Mineral-by-mineral listing of resources. Production, reserves, geology.*

Annual Report of the Uganda Protectorate Geological Survey Department for the Year Ended 31st December, 1943. Pp. 53; tbls. 2. *Description of year's field and office work on areal mapping, economic geology, water supply (including bore-hole details).*

Origem das Rochas Alcalinas (Origin of the Alkaline Rocks). DJALMA GUIMARÃES. Pp. 102; figs. 11; photos 12; tbls. 10. Estado de Minas Gerais, Instituto de Tecnologia Industrial Bol. 5. Belo Horizonte, 1947.

Brasil: Ministério da Agricultura, Departamento Nacional da Produção Mineral, Laboratório da Produção Mineral, Rio de Janeiro, 1945–46.

Bol. 19. Estanho (Tin). L. GATTI, A. GUERREIRO. Pp. 79; tbls. 12; photos 10; flow-sheets 9; figs. 4. *General information on tin mining, milling and smelting in Brasil.*

Bol. 20. Relatorios do Diretor (1943–1945) (Report of the Director). M. DA SILVA PINTO. Pp. 39.

Bol. 21. A Tantalita do Nordeste, sua Exportação e Analise (Tantalite of the Northeast, its Exportation and Analyses). MORRIS SLAVIN, C. M. PINTO, M. DA SILVA PINTO. Pp. 75; tbls. 9. *Improved methods of quantitative analysis of Ta_2O_5. 2 flow sheets. Graph showing tantalite specific gravity—Ta_2O_5 percent relationship.*

Bol. 22. Sinterização (Sintering). F. E. NOÉ. Pp. 94; figs. 9; 3 flow-sheets. *Detailed description of 8 U. S. concentrating and sintering plants.*

Bol. 23. Beneficiamento de Minerios de Cromo. (Beneficiation of Chromium Minerals). R. B. TRAJANO, J. B. DE ARAUJO. Pp. 95; tbls. 18; flow-sheets 6. *Concentration experiments on various Brazilian chromite ores. Usual difficulty of inverse relationship of concentrate grade and recovery.*

The Gabbro Rocks Found near Gorumahisani Pahar, Mayurbhanj State, Orissa, and the Origin of the Associated Magnetic Deposits. S. C. CHATTERJEE. Pp. 28; figs. 16; map 1. Proc. of the Nat. Inst. of Sci. of India, vol. XI, No. 3. Calcutta, 1945. *Source of titaniferous and vanadiferous magnetite, ranging from norites to anorthosites, and some peridotites and pyroxenites. Detailed petrographic study. Magnetite of two generations, the last being late magmatic, formed from a magnetite rest magma.*

A Magyar Bauxitelöfordulások Földtani Alkata. E. VADÁSZ. Pp. 113; figs. 24. Magyar Állami Földtani Intézet Évkönyve 37 Kötet, 2 Füzet. Budapest, 1946. *Description of structure, mineralogy, lithology of principal Hungarian bauxite deposits. Author finds evidence of considerable movement of material before burial. Some are lower Cretaceous, others are post-Cretaceous, pre-Eocene. Text in Hungarian and German.*

Mémoire Explicatif de la Carte Géologique du Basin Houiller de Djerada et de la Région au Sud d'Oujda (Maroc Oriental Français). BORIS OWODENKO. Pp. 168; pls. 5, incl. colored geol. map, scale 1:100,000. Société Géologique de Belgique, Tome 70, Mémoires. Liège, 1947. *Stratigraphy, paleontology, structure of new (1927) coal basin in Djerada, Eastern French Morocco.*

SCIENTIFIC NOTES AND NEWS

DUNCAN MCCONNELL, formerly head of the Petrographic Laboratory of the U. S. Bureau of Reclamation at Denver, has recently accepted a position as head of the Sections in Inorganic Geochemistry and Petrography of the Geology Division of the Gulf Research & Development Company at Pittsburgh.

JOHN H. WEITZ has been appointed assistant professor of geology at Lehigh University, Bethlehem, Pa., and is teaching mineralogy, structural geology, and mineral resources.

Q. J. HENDERSON has been appointed senior geologist, North Broken Hill, Ltd., Broken Hill, N. S. W. He was formerly with the Tasmania Department of Mines.

A. C. SKERL, consulting geologist for Quebec Gold Mining Corporation, has completed geological mapping of the Cariboo Gold Quartz Mine and is now doing similar work at the Pellaire mine.

LAURENCE L. SMITH has been designated Acting State Geologist of South Carolina.

RAYMOND F. ROBINSON has resigned as geologist for the Federal Mining and Smelting Co., Wallace, Idaho, and has accepted the position of resident geologist for Sunshine Mining Co., Kellogg.

EDWARD H. WISSER, consulting geologist, San Francisco, has accepted the professorship of mining, Division of Mineral Technology, University of California, Berkeley, Calif.

A. S. FURCRON, assistant geologist of the Georgia Department of Mines, Mining and Geology, has been elected president of the Georgia Mineral Society to succeed DR. LANE MITCHELL of Georgia Tech.

NEWTON B. KNOX, mineral economist of Washington, D. C., has been appointed adviser to the Peruvian Government, with headquarters in Lima.

STEPHEN TABER has retired as head of the University of South Carolina geology department and as State Geologist to devote his full time to research work. He has served in the geology department for 35 years and has been State Geologist since 1913. Dr. Taber has been succeeded by DR. LAURENCE L. SMITH.

M. B. RAMACHANDRA RAO has returned to India, where he is geologist and geophysicist for the Mysore Geological Survey. For the last nine months he had been visiting various mining company operations in the U. S. and Canada.

PAUL M. TYLER terminated his work at MIT at the end of August to undertake general consulting work. For some weeks he has had his headquarters at the N. J. State Bureau of Mineral Research, New Brunswick, which he organized a couple of years ago.

ROBERT HALET has returned to Toronto from British Guiana where he had been carrying on geological investigations for the Kennco Company.

The Pan-American Institute of Mining Engineering and Geology announces the following tentative program for its meeting in New York in conjunction with the A.I.M.E. on Wednesday, February 18, 1948.

Morning Meeting—Presiding W. D. Johnston, Jr. and T. H. Miller.

9:30–10:30 Business Meeting, Reports by officers and chairmen of various committees.

10:30–12:00 First technical session: Papers as follows:

1. "Magnetite Deposits of Brazil," Alfred Bodenlos.
2. "Coal Mining in Brazil," Thomas Fraser and John Good.
3. "The New Rio Turbio Coal Field, Patagonia, Argentina," Angel V. Borrello. (Member of the Argentine Section.)
4. "Review of the Mining Industry of Latin America," Sumner M. Anderson.

Luncheon Meeting.

12:15–2:00 Speaker, Paul H. Daniels, Chief, Office of American Republics Affairs, Dept. of State. Subject: Report of the U. S. Delegation to the 2nd Pan American Congress of Mining Engineering and Geology, Rio de Janeiro, October, 1946.

Afternoon Meeting—Presiding Francis Cameron and G. M. Knebel.

2:30–5:00 Second technical session. Papers as follows:

5. "Geological Survey—Bureau of Mines Activities in the Other American Republics," J. S. McGrath.
6. "Mineral Deposits of Colombia," Quentin Singewald.
7. "Manganese Deposits of Mexico," Parker D. Trask.
8. "Stratigraphic Studies in Brazil," Josué Camargo Mendes.
9. "Stratigraphy of Southern Brazil," MacKenzie Gordon.
10. "Geology of Sierra Negra, Ancash, Peru," John Straczek.
11. "Lateritic Soils in Hispañola," Samuel Goldich.

The Geological Society of America, along with its affiliates, the Mineralogical Society, Paleontological Society, Society of Economic Geologists and Society of Vertebrate Paleontologists, celebrated with the Geological Association of Canada (its first Meeting) the 105th anniversary of the Geological Survey of Canada (the 100th fell in war time) at its meeting in Ottawa, Ontario, December 29–31. The meeting was extremely well attended, and an opportunity existed for a much larger attendance by Canadians than usual. Among the well arranged programs were two sessions on Economic Geology, one on Engineering Geology, two on Mineralogy, one on Structure and Geophysics, two outstanding sessions on Geochemistry. The feature of the meeting was the symposium on the Origin of Granite, participated in by H. H. Read of London, A. F. Buddington, F. F. Grout, G. E. Goodspeed and N. L. Bowen. It was chiefly a magma origin vs. replacement origin; the former seemed to hold the floor. The symposium occupied the morning and discussion lasted all afternoon.

Outstanding among the addresses were, the Presidential Address on *Our Petroleum Resources,* by A. I. Levorsen; Presidential Address of the Mineralogical Society on *Role of Temperature in Geology,* by Martin Buerger; Presidential Address of the Paleontological Society on *Stratigraphical Paleontology,* by R. C. Moore; Presidential Address of the Society of Vertebrate Paleontologists on *Pushing back the History of Land Mammals in Western North America,* by Chester Stock; and Presidential Address of the Society of Economic Geologists on *The New Coal Age,* by George H. Ashley.

Some outstanding papers of particular interest to Economic Geologists were: *Geology of the Labrador Iron deposits,* by J. A. Retty and A. E. Moss; *Interpretation of Aeromagnetic Surveys,* by Victor Vacquier and N. C. Steenland; *Pinchi Lake Mercury Belt, Canada,* by J. E. Armstrong; *Hydrothermal Alteration at Santa Rita,* N. M., by Paul F. Kerr, C. M. Patterson and Robert Wright; *Structure of Kirkland Lake, Canada,* by Harold Hopkins; *Leduc Oil Field, Alberta,* by T. A. Link.

The Society's Penrose Gold Medal was awarded to Arthur L. Day, and the Roebling Medal of the Mineralogical Society was awarded to Paul Niggli, of Switzerland.

DRURY A. PIFER, formerly mine manager for De Beers Consolidated Mines, Ltd., Kimberly, South Africa, is now acting director of the School of Mineral Engineering at the University of Washington, succeeding DEAN MILNOR ROBERTS, retired.

ROGERS PEALE has taken a professional trip down to Nicaragua.

F. A. LINFORTH became recently assistant to E. S. MCGLONE, vice-president in charge of Anaconda's Western operations. Mr. Linforth was formerly assistant to the manager of mines of the Anaconda Copper Mining Co.

For 1948 the Society of Economic Geologists has elected president T. M. BRODERICK, chief geologist for the Calumet and Hecla Consolidated Copper Co., Calumet, Mich.

ROBERT H. CARPENTER is now associated with the geology department of the Colorado School of Mines, Golden, having left Stanford University.

Last September CHARLES S. BACON, JR., was appointed head of the department of geology and mineralogy at Case Institute of Technology, Cleveland.

F. S. TURNEAURE is now associate professor of geology at the University of Michigan, Ann Arbor.

At the Homestake Mining Co., Lead, S. Dakota, JAMES A. HARDOR is now chief geologist and A. L. SLAUGHTER took over as assistant chief geologist.

The Canadian Department of Mines and Resources has created a new technical and research unit, the Mines, Forests, and Scientific Services Branch, which will include all the basic research activities of the Department. W. B. TIMM, formerly director of the mines and geology branch of the Department, is now director of the new unit.

HORACE MOSES, general manager of Chino Mines Division, Kennecott Copper Corporation, since 1938 will retire next December. His successor is William H. Goodrich, general superintendent.

A. F. NETELBEEK of the Geological Institute, Amsterdam, Holland, announces that a successful meeting of the International Federation of Students of Geology and Mining was held in Amsterdam with representatives from Czecho-Slovakia, Finland, France, Great-Britain, Hungary and Sweden. Several Universities in the U. S. A., Africa and Australia were unable to come because of travel difficulties, while Belgium, Norway and Switzerland were prevented from coming at the last moment. It was decided that the congress will only be held every third year, but an extra session will be held in Hungary in the fall of 1948. Those wishing to particiate should inform Mr. Netelbeek prior to March 30, 1948.

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